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Organosilicon derivatives of boric acid - tris(trialkylsilyl) borates and polyborosiloxanes. organosilicon-boron; new compounds

M.G.Voronkov and V.N.Zgonnik (Silicate Chem.Inst., Leningrad). Zhur.Obshchei Khim. 27, 1476-85(1957).

Heating 32.7 g. Et_3SiOMe and 6.2 g. H_3BO_3 6 hrs. at reflux gave 8.7 g. MeOH and 30 g. $B(OSiEt_3)_3$, b_2 130-40°, b_{760} 310-12°; direct distn. of Et_3SiOMe from H_3BO_3 gave a 70% yield. Pure $(Et_3SiO)_3B$, b_{10} 178-9°, d_{20} 0.8918, n_D^{20} 1.4379. Similarly were prepd.: 73% $(MeEt_2SiO)_3B$, b_5 151-3°, 0.8751, 1.4382; and 74% $(MePr_2SiO)_3B$, b_1 157-60°, 0.8868, 1.4532. Heating 151 g. $(Me_3Si)_2O$ and 41.8 g. B_2O_3 in autoclave 27 hrs. at 350° gave 25 g. $(Me_3SiO)_3B$, b. 175-85°; pure product, b_{776} 184.5°, 0.8525, 1.3850. Refluxing 92.6 g. Me_3SiCl and 17.3 g. H_3BO_3 15 hrs. until HCl evolution ceased gave 20.6 g. (26.6%) crude $(Me_3SiO)_3B$, which after redistn. gave 12.8 g. pure product, b_5 48°, 0.8525, 1.3859. Similarly Me_3SiCl and H_3BO_3 gave 24.5% $(Et_3SiO)_3B$, b_{10} 178-9°. Heating 9.2 g. $(BuO)_3B$ and 16 g. Et_3SiOH and 0.2 g. Na with slow distn. gave 25.5% $(Et_3SiO)_3B$, b_4 142-9°. Slow distn. of 30.2 g. Me_2SiCl_2, 13.6 g. $(BuO)_3B$ and 0.3 g. dry $FeCl_3$ gave 11 g. BuCl and 10% $(Et_3SiO)_3B$, b_1 120-30°. Distn. of 25.5 g. $Me_2Si(OEt)_2$ slowly from 5.1 g. H_3BO_3 gave 12.3 g. EtOH and 5.5 g. $(EtO)_3B$, leaving a viscous polymer, which approximated $B_2O_3.4Me_2SiO$ compn. Distn. of 35.5 g. $MeSi(OEt)_3$ from 13.6 g. H_3BO_3 gave 87% EtOH and a polymer residue whose compn. was $B_2O_3.4MeSiO_{1.5}$. Distn. of 62.5 g. $(EtO)_4Si$ from 24.7 g. H_3BO_3 gave 89% EtOH and a polymer residue contg. 5% B and 28.9% Si; extn. with MeOH raised the Si content and lowered B content; heating the residue to 900° gave wt. loss indicative of elsavage of OEt groups. Refluxing 35.5 g. Me_3SiOEt with 6.2 g. H_3BO_3 6 hrs. gave EtOH, Me_3SiOMe, $(Me_3Si)_2O$ and 20 g. $(MeO)_3B$; same reaction with p-$MeOC_6H_4SO_3H$ catalyst also gave 3-7% $(Me_3SiO)_3B$. Distn. of 137 g. $Si(OMe)_4$ from 24.8 g. B_2O_3 gave 66% $(MeO)_3B$, b_{760} 67.5°, n_D^{20} 1.3678. Heating 12.4 g. H_3BO_3 and 32.7 g. Me_3SiCl gave a colorless polymer of $B_2O_3.4Me_2SiO$ compn., which hardens in air. Distn. of $(Me_3SiO)_3B$ from [illegible] gave 43% $(Et_3Si)_2O$.

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(21)

organoboron; Routine

Organoboron compounds. 17. Reaction of amine complexes of esters of diarylboric acids and organolithium compounds. Synthesis of unsymmetric triarylborons.

B.M.Mikhailov and V.A.Vaver (N.D.Zelinskii Inst.Org.Chem., Moscow). Izvest. Akad.Nauk S.S.S.R.Otdel.Khim.Nauk 1957, 818-7. Cf. this j.1956,451.

To a soln. of the complex from 10.01 g. iso-AmOBPh$_2$ and 3.[illegible] g. pyridine in 10 ml. Et$_2$O was added 8.75 g. 1-C$_{10}$H$_7$Li.Et$_2$O in 50 ml. Et$_2$O; after refluxing 4 hrs. the mixture was washed with H$_2$O and yielded on evapn. and diln. with MeOH 57.5% 1-C$_{10}$H$_7$BPh$_2$.C$_5$H$_5$N, dec.175-80°. Similarly iso-BuOBPh$_2$ and p-MeOC$_6$H$_4$Li gave 77% p-MeOC$_6$H$_4$BPh$_2$.C$_5$H$_5$N, m.156-8°(from dil.MeOH); 87% o-MeOC$_6$H$_4$BPh$_2$.C$_5$H$_5$N, m.177-9°(from aq. Me$_2$CO); 91% (1-C$_{10}$H$_7$)$_2$BPh.C$_5$H$_5$N, dec.215-7°; 77% (1-C$_{10}$H$_7$)$_2$BC$_6$H$_4$Me-o.C$_5$H$_5$N, m.203-5°; 72% (p-BrC$_6$H$_4$)$_2$B-C$_6$H$_4$Me-o.C$_5$H$_5$N, m. not given; [illegible] to 6.04 g. iso-BuOBPh$_2$.NH$_3$ was added 0.03 mole p-MeOC$_6$H$_4$Li and after 4 hrs. refluxing in Et$_2$O, the mixture gave 52% p-MeOC$_6$H$_4$BPh$_2$.NH$_3$, dec.180-91°(from C$_6$H$_6$); similarly was prepd. 48.5% (p-ClC$_6$H$_4$)$_2$BPh.NH$_3$, m.213-15°(from EtOH). Treatment of I with 30% H$_2$SO$_4$ in Et$_2$O under N$_2$ gave 49% p-MeOC$_6$H$_4$BPh$_2$, b$_3$170-5°, which solidifies on chilling. The above listed complexes can be also converted to the free R$_3$B by treatment with dry HCl in Et$_2$O; thus was prepd. p-MeOC$_6$H$_4$BPh$_2$ from the corresponding adduct with NH$_3$. Pyrolysis of (1-C$_{10}$H$_7$)$_2$BPh.C$_5$H$_5$N in a sausage flask at 175-85° gave 87.8% C$_5$H$_5$N and 45% (1-C$_{10}$H$_7$)$_2$BPh, m.146-8° b$_2$230-40°. Similarly was obtained (1-C$_{10}$H$_7$)$_2$BC$_6$H$_4$Me-o, b$_{0.05}$197-9°; [illegible] Ph$_3$B.NH$_3$ in Et$_2$O treated with dry HCl gave 62.5% Ph$_3$B; the pyridine complexes above can be also decomposed to R$_3$B by picric acid in C$_6$H$_6$.

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(22)

organochromium

Structure of organochromium compounds.

G.A.Razuvaev, Yu.A.Sorokin, G.A.Domrachev, G.G.Petukhov, Yu.D.Tsvetkov and Yu.N.Molin (State Univ., Gorky). Doklady Akad.Nauk S.S.S.R.113, 1293-4(1957).

Examn. of the properties of organo-Cr compounds reported by Seiss (Nature, Yale Sci.Mag. 29, 14(1955)) coupled with the fact that biphenylylchromium iodide and phenoxide on illumination with ultraviolet light yield Ph_2 and if the reaction is run in $CDCl_3$ the product contains 0.1-0.3%D. The result indicates that the halide or phenoxide units are ionically bound to the positively charged Cr ion between the 2 aryl radicals. Paramagnetic electronic resonance spectra of these compounds were detd.(one is shown) in aq. soln. The presence of fine structure and distribution of spectral intensity suggests that the unpaired electron interacts with the nuclei of H of the aromatic rings.

Synthesis and analytical properties of tetra(2-thienyl)boric and tetra(p-anisyl)boric salts of alkali metals.

organoboron

V.A.Sazonova, B.P.Serebryakov and L.S.Kovaleva (M.V.Lomonosov State Univ., Moscow). Doklady Akad.Nauk S.S.S.R.113, 1295-8(1957).

To 2-thienylmagnesium iodide from 8 g. RI was added 1.8 g. KBF_4 and when 2 layers formed, the mixture was filtered yielding 2.5 g. solid, which after washing with Et_2O was taken up in $MeNO_2$, filtered and treated with Et_2O yielding 36% $(C_4H_3S)_4BK$, crystals (from H_2O); metathesis this with Cs salts gave the corresponding Cs salt, less sol. in H_2O; similarly were prepd.: Rb salt, intermediately sol. in H_2O between K and Cs salts; Tl salt. p-$MeOC_6H_4MgI$ from 10 g. RI treated with 1.34 g. KBF_4 gave 25% $(p\text{-}MeOC_6H_4)_4BK$, dec.280-300°(from Me_2CO-Et_2O), sparingly sol. in H_2O; this treated with a little dil.HCl in Me_2CO gave di-(p-anisyl)boric acid, m. 104-5°, while treatment of the K salt with RbCl gave the Rb salt, dec.280°; CsCl similarly gave the Cs salt, dec.290°. All these 3 salts show low solv in H_2O, the Cs salt being least sol.

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Examination of reversibility of electro-reduction of some haloorganotin compounds on dropping mercury electrode.

M.K.Seikina and R.Sh.Nigmatullin. Uchenye Zapiski Kazan.Gosudarst.Univ. im. V.I.Ul'yanova-Lenina, 116, No.1, Obshcheuniv.Sbornik, 167-70(1956). Oscillographic polarography was used for exam. of reduction on Hg electrode of Et_2SnCl_2 (87% irreversible at pH 7, 91.3% at 0.1M NaOH); Et_3SnCl (73-6% irreversible at pH 1, and 80% in N NaOH), and Me_3SnI (81.3% irreversible at pH 1). Typical oscillograms are shown.

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(24) organotin

Dipole moments of complex compounds of tetravalent tin with some organic acids. XI.

O.A.Osipov, G.S.Samofalova and E.I.Glushko (State Univ., Rostov-on-Don). Zhur.Obshchei Khim.27, 1428-33(1957).

Dipole moments were detd. in C_6H_6 for the complexes shown (moments in D): $SnCl_4.2AcOH$, 6.38; $[SnCl_4.2AcOH]AcOH$, 7.23; $[SnCl_4.2AcOH].$ 3.44; $[SnCl_4.2ClCH_2CO_2H]ClCH_2CO_2H$, 3.67; $SnCl_4.2CCl_3CO_2H$ 2.09; $SnCl_4.3CCl_3CO_2H$, 1.89; $SnCl_4.2BzOH$, 5.73; $[SnCl_4.2BzOH]BzOH$, 6.16D. Thus interaction with 2 two molecules of an organic acid leads to a considerable increase of the dipole moment, but the addn. of a third molecule of the acid produces but little change, which fact indicates that the 3rd molecule of the acid is outside the inner sphere of the complex. The results indicate the non-existence of a complex $SnCl_4.3CCl_3CO_2H$.

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Reaction of di-m-nitrophenyl mercury and di-o-nitrophenylmercury with phenols.XIII.

V.F.Martynova (State Pediatr.Med.Inst.,Leningrad). Zhur.Obshchei Khim.27, 1056-8(1957). Cf. Izvest.Akad.Nauk SSSR, Otdel.Khim.Nauk 1955,1063.

Heating $(m\text{-}O_2NC_6H_4)_2Hg$ (I) or $(o\text{-}O_2NC_6H_4)_2Hg$ (II) with the indicated phenols at 130-50° in ampuls gave the following amounts of liberated Hg in 3 hrs., resp.: pyrogallol 68.7%, 30.7%; resorcinol 34.93%, 21.9%; p-aminophenol 10.75% and 8.79%; hydroquinone 9.5% and 8.21%; $p\text{-}ClC_6H_4OH$ 20.52% and 15.6%; $2,4\text{-}Cl_2C_6H_3OH$ 21.76% and 16.62%; $p\text{-}MeC_6H_4OH$ 8.63% and 6.7%; PhOH 3.56% and 0%; $p\text{-}O_2NC_6H_4OH$ 3.79% and 3.52%; o-isomer 0% and 0%; m-isomer 8.27% and 5.3%; $2,4\text{-}(O_2N)_2C_6H_3OH$, $2,4,6\text{-}(O_2N)_3C_6H_2OH$ and $2,4,6\text{-}Cl_3C_6H_2OH$ gave 0% Hg. The following organomercury compounds were isolated: $m\text{-}O_2NC_6H_4HgR$ (R shown): p-nitrophenol, m.238-40°,75%; 2,4-dinitrophenol, m.253-4°, 52.4%; 2,4,6-trinitrophenol, does not m.250°, 45%; p-chlorophenol, does not m.250°, 36%; 2,4-dichlorophenol, m.151-3°, 64.7%; 2,4,6-trichlorophenol, does not m.260°, 72.8%; resorcinol, does not m.260°, 40.2%; p-cresol, does not m.260°, 98%; $o\text{-}O_2NC_6H_4HgR$: p-nitrophenol, m.187-8°, 57.7%; 2,4-dinitrophenol, m.196-7°, 67.6%; 2,4,6-trinitrophenol, m.181-3°, 47.2%; p-chlorophenol, does not m. 260°, 40%; 2,4-dichlorophenol, m.148-9°, 64%; 2,4,6-trichlorophenol,m.210-11°, 75.1%; resorcinol, does not m.250°, 56.7%; p-cresol, m.185°, 71.4%. Symmetrization of $m\text{-}O_2NC_6H_4HgCl$ with KI gave $(m\text{-}O_2NC_6H_4)_2Hg$,does not m.220°; similarly the $(p\text{-}O_2NC_6H_4)_2Hg$ analog, m.202-4°, was prepd. from RHgCl by heating with Cu in pyridine. $m\text{-}O_2NC_6H_4HgCl$, m.232-5°; o-isomer,m.185°.

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✓ Synthesis, new method of preparation

Condensation of methyltrichlorosilane in a silent discharge.

D.M.Andreev (Silicate Chem.Inst., Leningrad). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 818-25.

Passage of silent discharge (24.5Kv at 50 cycles) through refluxing vapor of $MeSiCl_3$ (detailed diagram of app. is shown), in H_2 stream gave C_2H_2, $MeSiCl_2CH_2SiCl_3$, b.182-5°, $MeSiCl_2CH_2CH_2SiCl_3$, b.199-202° (Raman spectrum 127(1), 152(1), 198(1), 202(2), 298(10), 465(8), 695(5), 788(3), 1262(9), 1401(9), 2906(15), 2984(15)); the substance, m. about 5°. Higher boiling products were treated with MeMgBr and EtMgBr yielding Et_4Si, 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane, 2,2,5,5,7,7-hexamethyl-2,5,7-trisilaoctane, and a methylation product, $C_{16}H_{40}Si_4O$, b_8 175-80°, n_D^{20} 1.4768, d_{20} 0.8886. The probable reaction mechanism is discussed on chain basis with participation of H atoms and Me radicals. The possibility of prepn. of silanes with alternating Si-C atoms thus exists in this reaction.

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(27) Connection between chemical structure of carbo- and hetero-cyclic compounds and their scintillating activity.

N.A.Adreva, M.M.Koton, Yu.N.Panov and F.S.Florinskii (Institute for High polymers, Leningrad). Doklady Akad.Nauk S.S.S.R.113, 311-13(1957).

Over 60 org. compounds were examined as solid scintillators in polystyrene. Compounds exceeding the standard scintillator (terphenyl) were: 1,4-bis-(2(5-phenyloxazolyl)benzene) 105%, 2,5-diphenyloxazole 100-15%, 2(1-naphthyl)-5-phenyloxazole 105%. In general the results agree with those of Hayes et al (Nucleonics, 1338(1955), 14, 42(1956)). Anthracene is more effective than phenanthrene or acenaphthene; O-heterocycle is more active than N- or S-analogs. Diarylmethanes have low activity. MeO, Me, Br, AcNH show a declining activity series for substituents. m-Isomers are more active than p-isomers in anthracene group.

(28) Anionotropic rearrangement of substituted perfluoropropenes. organic

B.L.Dyatkin, L.S.German and I.L.Knunyants. Doklady Akad.Nauk S.S.S.R.115, 320-2(1957). (IA)

To 59 g. CF_2:$CFCF_2Cl$ in MeOH was added with cooling in presence of phenolphthalein at -15° MeONa from 4.6 g.Na in 100 ml. MeOH; after aq. treatment there was obtained 67% CF_2:$CFCF_2OMe$ (I), b.38.5°, n_D^{20}1.3000, d_{20}1.3883; this with Br_2 in the cold gave $CF_2BrCFBrCF_2OMe$, b.136°, n_D^{20}1.4060, d_{20}2.1136. This (10 g.) heated 5 hrs. at 100-5° with 4 ml. H_2SO_4 and 4 g. powd.glass gave 77% $CF_2BrCFBrCO_2Me$, b_{28}70.5°, 1.4380, 2.0698; aq.NH_4OH converted this to the amide, m.61.5-2.5°(from hexane). I stored in ampul several days isomerized to CF_3CF:CF[illegible], b.58-8.5°, 1.3045, 1.3605; this added Br_2 to described yield $CF_3CFBrCFBrOMe$, b_{736}134°, 1.4040, 2.0510, which hydrolyzed as (Cf. Izvest.Akad.Nauk SSSR, otdel.khim.nauk 1956,1355) earlier to 56% $CF_3CFBrCO_2Me$, b.101-6°, n_D^{20}1.3698, which with NH_4OH gave the amide, m.89.5-90.5°(from hexane). IA treated in the cold with 50% excess Et_2NH in Et_2O gave 47% CF_3CF:$CFNEt_2$, b_{40}56-9°, n_D^{20}1.3715, which hydrolyzed to CF_3CH-$CONEt_2$, $b_8$87.5-8°, n_D^{20} 1.3966. Neutralization of the unused amine in Et_2O s

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gave 61% $CF_3CFBrCOOEt_2$, b_{25} 98-9°, 1.4200, 1.5042, after treatment with H_2O.

Compounds Related to Teflon, one of the most stable polymers known

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Syntheses with 1,1,3,3-tetraalkoxypropanes. Preparation of the simplest heterocyclic compounds.

T.V.Protopopova and A.P.Skoldinov. Zhur.Obshchei Khim.27, 1276-9(1957). Cf.this j.27,57(1957).

To 6.1 g. $CO(NH_2)_2$, 110 ml. EtOH and 22 g. $CH_2(CH_2(OEt)_2)_2$,(I), was added 20 ml. concd.HCl; after standing overnight the mixture was concd. in vacuo yielding 72% 2-hydroxypyrimidine, [illegible] HCl salt, m.198-200°. This with NaOH gave 83% 2-hydroxypyrimidine, m.177-8°(from EtOAc). To 7.9 g. $CS(NH_2)_2$ in 18 ml. concd.HCl was added 22 g.I, yielding on standing overnight 89% 2-mercaptopyrimidine HCl salt, which with NaOH gave the free base, dec.217-8°(from H_2O). To 10 g. $HN:C(NH_2)_2$.HCl in 40 g.H_2O and 25 ml. concd.HCl was added over 1.5 hrs. 22 g.I; on the following day the mixture was evapd. and treated with NaOH yielding 82% 2-aminopyrimidine, m.123-4° (from C_6H_6). To 7 g. N_2H_4.HCl in 20 ml. H_2O and 5 ml. N HCl was added at 40-50° 22 g.I; after 1 hr. at 50° the mixture was concd. in vacuo, treated with concd.NaOH and extd.with Et_2O yielding 80% pyrazole, m.68-9o(after sublimation). To 5.8 g. semicarbazide HCl in 20 ml.H_2O was added 11 g.I yielding in 2.5 hrs. a ppt. of 75% pyrazole-1-carboxamide,m.140-1°(from EtOH); this heated with 3N HCl gave pyrazole. To 7.6 g. NH_2OH.HCl in 50 ml. H_2O and 5 ml. N HCl there was added at 50-60° 22 g.I and the mixture after 0.5 hr. on a steam bath was concd. by distn. into aq.$CdCl_2$ soln. The pptd. double salt was decomposed by hot H_2O and distd. into H_2O, the distillate being then satd. with NaCl to yield 72% isoxazole, b_{729} 93.5-4.5°, d_{20}1.0787. To a soln. from 11 g.I, 20 ml. 0.5N HCl there was added with cooling Et_3N (about 8 ml.) to give a basic reaction, followed by 4.5 g. cyanoacetamide in 20 ml. H_2O; after 1 hr. at room temp., 2 hrs. at 60° and 1 hr on a steam bath, the mixture was evapd. and extd. with EtOH-Et_2O, yielding a yellow crystalline mass of 57% 3-cyano-2-pyridone, m.224-5°(from EtOH).

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Organoboron compounds. 18. New method of synthesis of diarylborinic acids. B.M.Mikhailov and V.A.Vaver (N.D.Zelinskii Inst.Org.Chem., Moscow). Izvest. Akad.Nauk S.S.S.R. Otdel.Khim.Nauk, 1957, 989-91. Cf. this j.1956,451. To 0.2 mole PhMgBr was added with cooling 9 g. $(iso\text{-}BuOBO)_3$ in C_6H_6 and the mixture was refluxed 1 hr. and treated with 200 ml. 3.5% HCl; the org. layer was sepd. rapidly and evapd. rapidly in vacuo with minimum heating, yielding on addn. of Et_2O-hexane to the residue 8.3 g. phenylboronic anhydride, m.190-3°, while the mother liquor after evapn. and addn. of isopentane gave 51.6% $(Ph_2B)_2O$, m.130-1°. The combined distillates gave iso-BuOH and some H_3BO_3. Reaction of PhMgBr as above with $(C_6H_{11}OBO)_3$ and treatment of the crude product with xxx $HOCH_2CH_2NH_2$ gave 62% $Ph_2BOCH_2CH_2NH_2$, m.186-8° (crude), m.190-1°(from EtOH). Reaction of $(iso\text{-}BuOBO)_3$ with $1\text{-}C_{10}H_7MgBr$ gave similarly after treatment with 3.5% HCl 76.6% $(1\text{-}C_{10}H_7)_2BOH$, m.114-5°. Similar reaction of $p\text{-}MeC_6H_4MgBr$ and treatment of the crude product with $HOCH_2CH_2NH_2$ gave 41% $(p\text{-}MeC_6H_4)_2BOCH_2CH_2NH_2$, m.174.5-6°(from EtOH), along with 21.2% $p\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$, $b_{3.5}$ 127-8°, d_{20} 0.9106, n_D^{20} 1.4761. The use of 0.2 mole $o\text{-}MeC_6H_4MgBr$ and 0.05 mole $(iso\text{-}BuOBO)_3$ gave after esterification of crude reaction products with iso-BuOH 21% $o\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$, b_3 111-5°, and 42% $(o\text{-}MeC_6H_4)_2BOCH_2CHMe_2$, $b_{2.5}$ 151-3°, 0.9701, 1.5432. The latter ester is slowly oxidized by contact with air.

organogermanium

Reaction of direct synthesis, halogen exchange and photochemical chlorination of methylhalogermanes.

V.A.Ponomarenko and G.Ya.Vzenkova (N.D.Zelinskii Inst.Org.Chem., Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk, 1957, 994-8.

In direct synthesis of Ge derivs. from MeX and Ge (cf. Rochow, JACS 69, 1729(1947) and 70, 436(1948)) the yield of $MeGeX_3$ rises with increase of amount of Cu mixed with Ge or alloyed with Ge. With 4:1 Ge:Cu alloy MeBr gave at 450° Me_2GeBr_2, b_{746} 153°, d_{20} 2.1183, n_D^{20} 1.5268, and somewhat more $MeGeBr_3$, b_{750} 168°, 2.6357, 1.5778. Me_2GeCl_2 (740 g.) and MeMgBr gave 12% Me_3GeCl, b_{736} 98°, 1.2493, 1.4337 (cf. Rochow above), along with 25% I.

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organosilicon

Synthesis of 1-n-hexamethylvinylethylsiloxanes.

K.A.Andrianov and N.A.Kurashova (Inst.Hetero-Org.Compounds, Acad.Sci., Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 956-61.

EtMgBr from 24 g. Mg in Et_2O was treated with 166 g. $CH_2:CHSiCl_3$ in Et_2O yielding 28.9% $CH_2:CHSiEtCl_2$, b.127-8°, d_{20} 1.0416, n_D^{20} 1.4302 (I). To 180 ml. H_2O was added a mixture of 15.5 g. I and 21.72 g. Me_3SiCl at 38-50°, yielding 91.8% $Me_3SiOSiEt(CH:CH_2)OSiMe_3$, b_3 48-9°, 0.8421, 1.4011. Similarly 22 g. I and 18.21 g. Me_3SiCl gave with H_2O 20.9% $Me_3SiO(SiEt(CH:CH_2)O)_2SiMe_3$, b_5 98-110°, 0.8982, 1.4157. Similarly were obtained: 24.9% $Me_3SiO(SiEt(CH:CH_2)O)_3SiMe_3$, b_5 145-52°, 0.9235, 1.4215, and 9.2% $Me_3SiO(SiEt(CH:CH_2)O)_4SiMe_3$, b_5 171-90°, 0.9457, 1.4284. To 400 ml. H_2O at 80° was added 40.4 g. $CH_2:CHSiCl_3$ and 81.5 g. Me_3SiCl over 2.5 hrs. yielding 4.4% $CH_2:CHSi(OSiMe_3)_3$, b_4 135-40°, 0.9432, 1.4099. To 18.42 g. I was added 15 g. abs. EtOH and after heating finally to 70° 10 hrs. the mixture yielded 50.2% $CH_2:CHSiEt(OEt)_2$, b.149-52°, 0.8850, 1.4062; similarly was prepd. 24.8% $CH_2:CHSiEt(OMe)_2$, b_5 71-3°, 0.8609, 1.4146; and 45.7% $(iso\text{-}BuO)_2SiEtCH:CH_2$, b_4 60-1°, 0.8479, 1.4139. Reaction of I with AcONa in MePh at 70-80° similarly gave 56.42% $CH_2:CHSiEt(OAc)_2$, b_4 84-6°, 1.0216, 1.4165. Viscosity-temperature curves shown for the polysiloxanes listed above indicate similarity between the temp.coeffs. of these products and those of polymethylsiloxanes of linear structure; the energy of activation of viscous flow is somewhat higher for the 1st type.

organosilicon

Strength of silicon-carbon bond in chlorophenyltrichlorosilanes and chlorophenylethyldichlorosilanes.

K.A.Andrianov and V.A.Odinets (Inst.Hetero-Org.Compounds, Acad.Sci., Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 962-7.

Hydrolysis of $ArSiCl_3$, $ArEtSiCl_2$, in which Ar is m-chloro-, dichloro-, trichloro-, tetrachloro-, and pentachlorophenyl radical, in acidic or basic media merely gave the polysiloxanes expected of hydrolysis of the Si-Cl bonds; the Cl substituents in the ring were unaffected.

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Silico-organic esters of organo-silicon acids.

B.N.Dolgov, E.V.Kukharskaya and D.N.Andreev (Silicate Chem.Inst., Leningrad) Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 968-71.

Heating 14.6 g. $Me_3SiCH_2CH_2CO_2H$ (cf.Sommer et al.JACS 73,5833(1951)) with 24 g. Et_3SiO_2CEt 6 hrs. at 190-200° gave 41.9% $Me_3SiCH_2CH_2CO_2SiEt_3$, b_8 118-4°, d_{20} 0.8812, n_D^{20} 1.4372. Similarly was prepd. 59.5% $(Me_3SiCH_2CH_2CO_2)_2SiMe_2$, b_3 151.5°, 0.9407, 1.4368; 76.1% $MeEtSiCH_2CH_2CO_2SiEt_3$, b_2 137.5°, 0.8905, 1.4473; 58.8% [illegible] $(Et_3SiO_2CCH_2CH_2SiMe_2)_2O$, b_6 170-2°, 0.9213, 1.4405; and 37.1% $(Et_3SiO_2CCH_2CH_2SiEt_2)_2O$, b_1 178-81°, 0.9251, 1.4430. To di-Et Na-malonate from 42.6 g. Na in 1 l. abs.EtOH was added 280 g. $MeEt_2SiCH_2Cl$ and the reaction mixture treated as described by Sommer et al.(JACS 71, 1509(1949)) gave 63.2% $MeEt_2SiCH_2CH(CO_2Et)_2$, b_4 141°, 0.9681, 1.4408. This (314 g.) added dropwise in 1.5 hrs. to 255.4 g. KOH in 855 ml. H_2O at 90° then evapd. and treated with concd.HCl gave 75.3% $MeEt_2SiCH_2CH_2CO_2H$, b_6 138.5°, 0.9506, 1.4455. This (96.6 g.) added to 98 ml. concd.H_2SO_4 over 1 hr. and stirred 2 hrs. gave after treatment with ice 85.7% $(HO_2CCH_2-CH_2SiEt_2)_2O$, b_4 154-5°, 1.0556, 1.4648.

organosilicon

Synthesis and transformation of unsaturated organosilicon compounds. 5. Synthesis of mixed diacetylenic organosilicon glycols.

I.A.Shikhiev and L.A.Kayutenko (N.D.Zelinskii Inst.Org.Chem., Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 991-3. Cf. this J.1954,945. Reaction of 0.5 mole $Me_2C(OH)C{\equiv}CH$ with 1 mole EtMgI (unspecified) and treatment of the cooled mixture with 0.25 mole $MePhSiCl_2$ gave after refluxing 4 hrs. and treatment with cold dil.HCl 47.4% [illegible] m.139-50°; this hydrogenated over Raney Ni in EtOH to satd. analog, m.98-4°. I heated with Ac_2O gave the diacetate, b_4 178-9°, d_{20} 1.0281, n_D^{20} 1.5112. Similarly were obtained: 57.3% $HOCMe_2C{\equiv}CSiEtPhC{\equiv}CCMe_2OH$, m.92-3°; 43.7% $HOCMe_2C{\equiv}CSiPh_2C{\equiv}CCMe_2OH$, m.123-4°; 85.8% $HOCMe_2C{\equiv}CSiEtBuC{\equiv}CCMe_2OH$, m.62-3°; $HOCMe_2C{\equiv}CSiMe(C_{10}H_7)C{\equiv}CCMe_2OH$, m.98-9°.

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Mobility of fluoride ions of salts of fluosilicic acid dependent on the radii of their cations.

G.V.Medoks and E.M.Soshestvenskaya (Agr.Inst.,Saratov). Zhur.Obshchei Khim. 27, 1997-2000(1957). Cf. this j.27,172(1957).

Yields of tetra substituted silanes in the reaction of alkali fluosilicates with Grignard reagents are linearly dependent on the radii of cations. Thus treatment of PrMgBr with the Li salt, evapn. of Et_2O and heating the residue to 160-70°(exothermic reaction requires momentary cooling) gave after treatment with aq.HCl Pr_4Si(from 3.12 g. Li salt and 58 g. PrBr). The Na salt (3.76 g.) similarly gave 0.86 g. Pr_4Si; K salt (4.41 g.) gave 1.36 g. Pr_4Si and Rb salt (6.26 g.) gave 1.52 g. Pr_4Si. BuMgBr gave a similar set of results.

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A 22% yield of Me_3GeBr, b_{755} 115°, 1.5486, 1.4660, was obtained from 21.5 g. Me_3GeCl and MgClBr refluxed 10 hrs. in Et_2O. Reaction of 41 g. $MeGeCl_3$-CH_2Cl with MeMgI from 10 g. Mg gave in Et_2O 24% Me_3GeCH_2I, b_{752} 154°, 1.7160, 1.5112. An 18.5% yield of Cl_3GeCH_2Cl, b_{759} 149°, 1.8415, 1.5005, was formed from 131 g. Cl_3GeMe under conditions described by Ponomarenko and Mironov, Doklady Akad. Nauk SSSR 94, 485 (1954). Similar chlorination of 51 g. $MeGeCl_3$ gave 17 g. Cl_3GeCCl_3, b_{200} 150°, m. 106-7°. Similarly chlorination of 193 g. Me_2GeCl_2 gave 73.5 g. $MeGeCl_2CH_2Cl$, b_{750} 155°, 1.6694, 1.4930. The Swarts reaction of corresponding chlorides or bromides gave Me_3GeF, b_{746} 76°, 1.2300, 1.3863, and Me_2GeF_2, b_{750} 112°, 1.3726, 1.3743.

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Reaction of ethylene oxide and cyclohexene oxide with organochlorosilanes. M.S.Malinovskii and M.K.Romantsevich(State Univ.,Lvov). Zhur.Obshchei Khim. 27, 1873-6(1957).

Reaction of olefin oxides with chlorosilanes yields β-chloroalkoxy derivs. Into 25.8 g. $EtSiHCl_2$ in dry Et_2O was introduced dry ethylene oxide yielding 80% $EtSiH(OCH_2CH_2Cl)_2$, b_3 86.5-8°, n_D^{20} 1.4464, d_{20} 1.1585; similarly were prepd.: 75.7% $EtBuSiH(OCH_2CH_2Cl)$, b_3 50°, 1.4349, 0.9267; 79.7% $ClCH_2SiMe(OCH_2CH_2Cl)_2$, b_3 109°, 1.4671, 1.3671; 75.5% $Cl_2CHSiMe(OCH_2CH_2Cl)_2$, $b_{2.5}$ 117-8°, 1.4795, 1.3454; 68.3% $EtSi(OCH_2CH_2Cl)_3$, $b_{3.5}$ 133-4°, 1.4597, 1.2569; 75.3% $Et_2Si(OCH_2CH_2Cl)_2$, b_4 96-7°, 1.4526, 1.1011; 87.5% $EtPhSi(OCH_2CH_2Cl)_2$, b_3 98-9°, 1.5043, 1.0582; 76.4% $Me_2PrSiOCH_2CH_2Cl$, b_{15} 71-2°, 1.4331, 0.9472; 59.2% $Me_3SiOCH_2CH_2Cl$, b_{52} 72-3°, 1.4293, 1.3814. Similar reaction of cyclohexene oxide, requiring 10 hrs. at 60° for completion, gave: $MeSi(OC_6H_{10}Cl\text{-}o)_3$, 70.3%, $b_{2.5}$ 211-4°, 1.4971, 1.1806; 73.4% $Me_2Si(OC_6H_{10}Cl\text{-}o)_2$, $b_{2.5}$ 152-4°, 1.4844, 1.1178; 68.7% $Me_3SiOC_6H_{10}Cl\text{-}o$, b_3 60-1.5°, 1.4565, 0.9931; 75.2% $MeSiH(OC_6H_{10}Cl\text{-}o)_2$, b_3 136-7°, 1.4865, 1.1404; 94.2% $Si(OC_6H_{10}Cl\text{-}o)_4$, m.47-51°. The chloroethyl derivs. are rapidly hydrolyzed by H_2O especially in presence of acids. The reaction with ethylene oxide has an appreciable induction period.

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organosilicon

Synthesis and dehydration of unsaturated silicon-bearing alcohols. A.D.Petrov, L.L.Shchukovskaya, G.I.Sidyk-Sadd and Yu.P.Egorov. (N.D. Zelinskii Inst.Org.Chem.,Acad.Sci.,Moscow). Doklady Akad.Nauk S.S.S.R. 118 532-5(1957). cf. this j.118, 79(1957)

Heating 18 g. ethynylcyclohexanol and 18 g. Et_3SiH in the presence of Pt-C in autoclave 24 hrs. at 200-10° gave 90% $(CH_2)_5C(OH)CH_2SiEt_3$, b_{20} 100.5-70.5°, n_D^{20} 1.4575, d_{20} 0.9168. Treatment of 18 g. ethynylcyclohexanol with Et Mg from 7.8 g. Mg, the reaction mixture being then treated with 57 g. Et_3SiBr and heating 8 hrs. to 150° gave 42% $(CH_2)_5C(OH)CH_2SiEt_3$, b_{22} 161.5-2°, 1.4555, 0.9120, similarly were prepd.: 50% $Me_3SiCH_2CH_2CMe_2OH$, $b_{10.5}$ 86.5°, 1.4510, 0.8980; 40% $Me_3SiCH_2CMe_2OH$, b_{12} 84°, 1.4515, 0.8860; $(CH_3)_2C(OH)C(CH_3)_2SiEt_3$, b_{22} 137°, n_D 71.5-0.5°; and $Me_3SiCH_2CMe_2OH$, b_{760} 132°, n_D 117.5-6.5°. Treatment of $Me_2C(OH)CH$ in pyridine with Me_2SiCl_2 subjecting 1.5 hrs. at 100° gave $Me_2C(OH)CH_2SiMe_2$, b_{760} 128.7-4.5°, b_{20} 58.5°, 1.4510, 0.8614 (the isomeric tertiary alc., b_{20} 121.5°, 1.4387, 0.8884, was previously reported as being the above other; cf. Petrov et al. this j. 95, 826(1954)). Dehydration of the alco. with $KHSO_4$ readily yielded the following unsatd. compounds: 80% $Me_2SiCH_2CH_2CMe_2OH$, b_{760} 150°, 1.4518, 0.7897; 90% $Me_3SiCH_2CMe_2OH$, b_{760} 141.5-2°, 1.4521, 0.7940; 75% $Me_3SiCH_2CMe_2OH$, b_{20} 56-7°, 1.4390, 0.8007; 70% 1-cyclohexenyl-1-triethylsilylethene, b_{24} 141.5-2.5°, 1.5020, 0.8911. Infrared spectra of the products are discussed; with adjacent location of the ethynyl bond and of the characteristic band in 2170-2100 cm^{-1}; with conjugation of ethynyl and ethylenic bonds this changes to about 2150 cm^{-1}; location of this in the end of the chain gives the band at 2118 cm^{-1}, which is close to that in 1-alkynes. The alco. with CH_2CH termination show a band at 3287 cm^{-1} and the typical OH band at 2.78 μ.

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Electronic paramagnetic resonance in some organochromium compounds with sandwich structures.

Yu.D.Tsvetkov, V.V.Voevodskii, G.A.Razuvaev, Yu.V.Serokin and G.A.Domrachev (State Univ., Gorkii). Doklady Akad.Nauk S.S.S.R.115, 118-21(1957).

Traces of paramagnetic resonance spectra are shown for sandwich-type compounds of Cr: $Cr(C_6H_6)_2I$, $Cr(Ph_2)_2I$, $Cr(Ph_2)_2OPh$. The 1st 2 compounds have asymmetric absorption, with replacement of I by OPh eliminating the asymmetry. The following g-factors and $\Delta H_{1/2}$(oerst) are given, resp. for these substances: 1.975, 38; 1.987, 28; 1.993, 26. The half-widths of the absorption lines were 17 oerst. for all three, as shown above. Fine structure was shown in spectra of the last 2 substances only. This can be explained by localization of unpaired electron and pos.charge at the Cr atom or at the aromatic components.

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Organosilicon

Synthesis and properties of mono-, di-, and tri-p-tolylalkylsilanes. N.S.Nametkin, A.V.Topchiev, Gu Shan-Li and N.A.Lecnova (L.M.Gubkin Petrol. Inst., Moscow). Doklady Akad.Nauk S.S.S.R.115, 107-9(1957).

The following tolylsilanes were prepd. by the reaction of p-MeC_6H_4Li or corresponding Grignard reagent with the appropriate halosilane or ethoxysilane by heating 10 hrs. at about 100°. The trialkyl deriv.s were prepd. from alkyl-lithium reagents and appropriate halosilanes. The yields were generally about 40-70%. Reported are: (R=p-MeC_6H_4): $RSiMe_3$, b_{750} 190-5°, d_{20} 0.8851, n_D^{20} 1.4900; $RSiEt_3$, b_3 88-9°, 0.8907, 1.5025; $RSiPr_3$, b_4 121-2°, 0.8764, 1.4952; $RSiBu_3$, b_3 154-6°, 0.8706, 1.4928; $RSiAm\text{-}iso_3$, b_3 168-89°, 0.8649, 1.4888; R_2SiMe_2, b_3 128-30°, 0.9709, 1.5530; R_2SiEt_2, b_3 145-7°, 0.9645, 1.5530; R_2SiPr_2, b_4 178-80°, 0.9502, 1.5428; R_2SiBu_2, b_3 194-5°, 0.9400, 1.5373; $iso\text{-}Bu_2SiR_2$, b_3 174-6°, 0.9405, 1.5345; $iso\text{-}Am_2SiR_2$, b_3 180-2°, 0.9304, 1.5308; $RSiPr_2OEt$, b_3 98-100°, 0.9159, 1.4897; $RSi(OEt)Bu\text{-}iso_2$, b_3 137-8°, 0.9088, 1.4888; $RSi(OEt)_3$, b_7 115-7°, 0.9852, 1.4464; $R_2Si(OEt)_2$, b_4 150-2°, 1.0148, 1.5068; R_3SiMe, b_4 127-30°, m.91.5-2.5°; R_3SiEt, b_3 190-2°, m.72°; R_3SiPr, b_4 206-8°, m.84.3-5°; R_3SiBu, b_4 214-6°, 47.5-8°; $iso\text{-}Bu_3SiR$, b_3 197-9°, m.68-9°; $iso\text{-}Am_3SiR$, b_3 208-7°, 49-50°; R_3SiOEt, b_3 194-5°, m.50-50.5°.

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Synthesis of polymethylidimethylsiloxanes.

K.A.Andrianov and V.M.Mantrova (Electrotech.Inst.,Moscow). Zhur.Obshchei Khim.27, 1243-9(1957).

Heating 46 g. $Me_2Si(OEt)_2$, 7.5 g. Me_2SiCl_2 and 0.25 g. $FeCl_3.6H_2O$ to 140° until Cl content of the mixture dropped to 3-4% gave 86-8% viscous polymer Anhydrous catalyst gave 93-4% polymer, but the hexahydrate gave the most rapid reaction. Hydrolysis of the product and fractionation of the polymer showed that some 50% of the polymer has mol.wt. 900-1100. The mol.wt. distribution varied with the detailed conditions of the condensation. The formation of the polysiloxanes is discussed in light of probable intermediate formation of appropriate silanols, produced by hydrolytic action of H_2O from the hydrated catalyst.

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Preparation of alkylalkoxysilanes from organosiloxanes.

M.G.Voronkov (Silicate Chem.Inst.,Leningrad). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 882.

Conversion of organosiloxanes into alkylalkoxysilanes was attained by refluxing the desired ROH with the siloxane in presence of MePh or C_6H_6 with azeotropic continuous removal of H_2O formed in the reaction, or with the use of a dehydrating agent. Direct distn. of mixtures of linear or cyclic siloxanes with $(RO)_4Si$ in presence of KOH also gave $RSi(OR)$ derivs. Yields are 50-90% and a series of $R_nSi(OR)_{4-n}$ compounds was prepd. No details are given.

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Reaction of [illegible] acid and of methylethoxychlorosilanes. organosilicon

K.A.Andrianov, S.A.Golubtsov, T.S.Maklashina and N.P.Lobusevich. Zhur. Obshchei Khim.27, 914-17(1957).

Addn. of 103.5 g. dry EtOH to 255 g. $SiCl_4$ 2-3 hrs. at 18-20°, followed by 2 hrs. heating finally to 115° gave 258.5 g. mixed chloroethoxysilanes. This mixture (150 g.) was slowly added with cooling in 327 g.MePh and 3 ml. Et_2O to 44.5 g. Mg shavings preactivated with 3 ml. EtCl and 3 ml. Et_2O; the addition (4-5 hrs.) was followed by 2-3 hrs. at 100°, and treatment with aq.HCl at 30-40°, yielding on evapn. of the org. layer a residue of polyethylsiloxane mixture. The yields ranged from 44% to 74% in separate expts., tending to be higher with larger amounts of EtOH in the 1st step. Similar reaction of $MeSiCl_3$ and MeOH followed by the reaction with Mg and EtCl, described above, gave polymethylethylsiloxane mixtures in up to 95% yields on $SiCl_4$. The best yield of the polysiloxane results when 40-50% of Cl content of $SiCl_4$ is esterified in the 1st step; the same proportion is correct for $MeSiCl_3$ also.

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Reaction of epichlorohydrin and methyl glycidyl ether with organochlorosilanes.

M.S.Malinovskii and M.K.Romantsevich (State Univ.,Lvov). Zhur.Obshchei Khim.27, 1680-5(1957). Cf.Sbornik Statei po Obshchei Khim.2,1366(1955). Reaction of chlorosilanes with epichlorohydrin results in ring opening at the secondary C atom. Addn. of 29.76 g. epichlorohydrin to 14.95 g. $MeSiCl_3$ at 30-5° and heating 10 hrs. at 60° gave 77.3% $MeSi(OCH(CH_2Cl)_2)_3$ (I), b_3 202-4°, n_D^{20} 1.4912, d_{20} 1.3894. Similarly were prepd.: 62.2% $Me_3SiOCH(CH_2Cl)_2$, b_{68} 105-7°, 1.4394, 1.0762; 76.2% $Me_2Si(OCH(CH_2Cl)_2)_2$, b_3 135-7°, 1.4771, 1.2791; 87.5% $MeSiH(OCH(CH_2Cl)_2)_2$, $b_{3.5}$ 132°, 1.4802, 1.3124; 75.5% $Et_2Si(OCH(CH_2Cl)_2)_2$, b_2 136-8°, 1.4786, 1.2552; 77.5% $EtSi(OCH(CH_2Cl)_2)_3$, b_2 191-3°, 1.4915, 1.3634; $EtSiH(OCH(CH_2Cl)_2)_2$, $b_{3.5}$ 139°, 1.4799, 1.2805. I treated with $Na_2Cr_2O_7$ in xxxH aq.H_2SO_4 gave $CO(CH_2Cl)_2$. Reaction with Et_3SiCl failed to take place. Reaction of Me glycidyl ether (27.45 g.) with 14.95 g. $MeSiCl_3$ gave 29.3% $MeSi(OCH(CH_2Cl)CH_2OMe)_3$, b_3 170-70.5°, 1.4579, 1.2054. Similarly were prepd.: 71.4% $Me_2Si(OCH(CH_2Cl)CH_2OMe)_2$, b_5 119.5-20°, 1.4495, 1.1321; 77.1% $Me_3SiOCH(CH_2Cl)CH_2OMe$, b_{30} 86.5-8°, 1.4273, 0.9956; 76% $MeSiH(OCH(CH_2Cl)CH_2OMe)_2$, b_5 118.5-20°, 1.4495, 1.1491; 72.8% $EtSi(OCH(CH_2Cl)CH_2OMe)_3$, b_4 131-3°, 1.4599, 1.1968; 66.4% $Et_2Si(OCH(CH_2Cl)CH_2OMe)_2$, b_4 137-8°, 1.4588, 1.1202; 72.5% $EtSiH(OCH(CH_2Cl)CH_2OMe)_2$, b_4 128-30°, 1.4513, 1.1396. The structure of the products was confirmed by oxidation as above to $MeOCH_2COCH_2Cl$ and reduction of this with Zn-AcOH to $MeOCH_2Ac$, b_{758} 117°, d_{20} 0.9558. The previous report by Andrianov et al (Izvest.Akad.Nauk SSSR, otdel.khim.nauk 1955,531) as to orientation of the reaction of epichlorohydrin with chlorosilanes is severely criticized.

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Synthesis of liquid (m-l)hexamethylpolychlorophenylethylsiloxanes.

K.A.Andrianov and V.A.Odinets (Inst.Hetero-org.Compounds, Moscow). Izvest. Akad.Nauk S.S.S.R.1957, 684-91.

It was shown that liquid polysiloxanes bearing Et and chlorophenyl groups on the Si atoms have higher dielectric properties than their Et-Ph analogs and that increase of Cl content in the Ph radicals and increase of the number of Si atoms in the polymer serve to improve the dielectric permeability. In the temp. range 0-120° the activation energy of viscous flow in the present group of polysiloxanes is much higher than in corresponding Me_2 analogs; the activation energy increases with the number of Cl atoms in the Ph radicals and with the number of Si atoms in the polymer, as estd. from the temp. coeffs. of viscosity. To 400 g. H_2O and 100 g. MePh was added 100 g. m-$ClC_6H_4SiEtCl_2$, 108.5 g. Me_3SiCl and 100 g. MePh at reflux over 2-3 hrs.; after washing the org. layer was fractionated yielding $Me_3SiOSiEt(C_6H_4Cl\text{-}m)OSiMe_3$, $b_3$120-30°, n_D^{20}1.4854, d_{20}1.0541, η_{20}/η_{120} 7.0, ϵ 3.46. Similar reaction but with 55 g. Me_3SiCl gave a product which was undistillable; it was purified by contact with activated clay at 170° and gave 61% $Me_3SiO(SiEt(C_6H_4Cl\text{-}m)O)_2SiMe_3$, n_D^{20}1.5002, d_{20}1.0834, η_{20}/η_{120} 9.73, ϵ 3.61; use of 36 g. Me_3SiCl gave $Me_3SiO(EtSi(C_6H_4Cl\text{-}m)O)_3SiMe_3$, 70%, n_D^{20}1.5030, d_{20}1.1206, 11.6, 3.80; 30 g. Me_3SiCl gave $Me_3SiO(SiEt(C_6H_4Cl\text{-}m)O)_4SiMe_3$, 70%, 1.5098, 1.1357, 28.89, 3.96. Similar reaction of 90 g. $Cl_2C_6H_3SiEtCl_2$ (b_{10}150-2°, prepd. by chlorination of $PhEtSiCl_2$) and 86 g. Me_3SiCl gave 69% $Me_3SiOSiEt(C_6H_3Cl_2)OSiMe_3$, 1.4963, 1.1176, 10.46, 3.41. Similarly were obtained: $Me_3SiO(SiEt(C_6H_3Cl_2)O)_2SiMe_3$, 1.5118, 1.1636, 25.68, 3.56; $Me_3SiO(SiEt(C_6H_3Cl_2)O)_3SiMe_3$, 1.5250, 1.1851, 62.27, 3.64; $Me_3SiO(SiEt(C_6H_3Cl_2)O)_4SiMe_3$, 1.5350, 1.2020, 97.49, 3.73; $Me_3SiO(SiEt(C_6H_2Cl_3)OSiMe_3$, 1.5150, 1.2012, 18.53, 3.77; $Me_3SiO(SiEt(C_6H_2Cl_3)O)_2SiMe_3$, 1.5280, 1.2507, 50.45, 3.86; $Me_3SiO(SiEt(C_6H_2Cl_3)O)_3SiMe_3$, 1.5316, 1.3398, 326.69, 3.96; $Me_3SiO(SiEt(C_6H_2Cl_3)O)_4SiMe_3$, 1.5470, 1.5435, -, 3.98. The dichlorosilane used in the last series was prepd. by trichlorination of the $PhSiCl_3$; the dichlorosilane, b_{12}142-4°.

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New halogen containing aluminosiliconorganic compounds of type $R_3SiOAlX_2$. N.F.Orlov (Silicate Chem.Inst.,Leningrad). Doklady Akad.Nauk S.S.S.R.114, 1033-5(1957).

Cf. Voronkov et al. this j. 84,959(1952).

Heating equimolar proportions of hexaalkyldisiloxanes with AlX_3 with distn. of trialkylhalosilane results in 70-85% yields of $R_3SiOAlX_2$. Heating 43.6 g. $(MeEt_2Si)_2O$ and 26.6 g. $AlCl_3$ 1 hr. at 135°, finally at 210°, gave 24 g. $MeEt_2SiCl$ distillate while the residue gave 36 g. $MeEt_2SiOAlCl_2$, b_4 143-7°, m.33°. Similarly were obtained: $Me_3SiOAlCl_2$, b_4 102°, m.88°; $Me_2EtSiOAlCl_2$, b_4 125°, m.46.5°; $Et_3SiOAlCl_2$, b_4 173°, m.45°; $Me_3SiOAlBr_2$, b_4 127°, m.113.5-3°; $EtMe_2SiOAlBr_2$, $b_{2.5}$ 150°, m.66°; $MeEt_2SiOAlBr_2$, $b_{3.5}$ 173°, m.55°; $Et_3SiOAlBr_2$, b_3 181°, m.75°. The products are stable in dry air but react vigorously with H_2O; they are sol. in usual org. solvents. A similar reaction with $(Cl_3Si)_2O$ and AlX_3 failed to take place after several hours of refluxing. Slow addn. of $Me_3SiOAlCl_2$ to H_2O gave $(Me_3Si)_2O$.

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Reaction of silicon tetrachloride with acetic and benzoic anhydrides. V.V.Udovenko and Yu.Ya.Fialkov (Polytech.Inst.,Kiev). Zhur.Obshchei Khim.27, 905-6(1957). Cf. Friedel et al. Ann.145,177(1868). Mixing 1 mole $SiCl_4$ with 4 moles Ac_2O yields a ppt. of 80% $Si(OAc)_4$, m.110°, and AcCl. The same products form with other reactant proportions, but the product fails to precipitate if the ratio is under 1:4. Similar reaction with Bz_2O completed by 1 hr. on a steam bath and removal of BzCl in vacuo gave a viscous liquid $Si(OBz)_4$ which slowly solidified. This was undistillable.

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Synthesis of polyorganoalumosiloxanes. Reaction of metathesis of sodium salts of alkylsilanetriols and aluminum chloride.

K.A.Andrianov and A.A.Zhdanov (Inst.Hetero-org.Compounds, Acad.Sci., Moscow). Doklady Akad.Nauk S.S.S.R.114, 1005-7(1957).

Hydrolysis of 106 g. $PhSiCl_3$ in 100 ml. Et_2O with 200 ml.H_2O and 100 ml. Et_2O gave after sepn. and evapn. of the org.layer a polymer which after drying at 60-80° was treated with 100 ml. 20% NaOH in EtOH (exothermic) the soln. was evapd. and the residue dried in vacuo, yielding after recrystallization from 98% Me_2CO-2% H_2O, a solid $PhSi(OH)_2ONa.1.37H_2O$, (I). Stirring 37 g. $(Me_2SiO)_4$ cyclosiloxane with 20 g. NaOH in 50 ml. MeOH 3 hrs. at 40° gave after removal of volatiles and drying of the residue at 150°, a hygroscopic powder which treated in Me_2CO suspension with 4 moles H_2O per 1 mole of product, heated rapidly to boiling, filtering rapidly and cooling, gave needles of $NaOSiMe_2OSiMe_2ONa.4H_2O$. Similarly was prepd. $EtSi(OH)_2ONa.2H_2O$ (II) (from EtOH); and $NaO(SiPhMeO)_3Na$. (III) I (0.075 mole) in 130 ml. EtOH was treated with 0.025 mole $AlCl_3$ in 35 ml. EtOH and after refluxing 10 hrs. and filtration there was obtained 77.8% NaCl while the filtrate gave a hard polymer approximating $(PhSiO_2)_3Al$. Similarly II gave an organically soluble polymer $(EtSiO_2)_3Al$ and III similarly gave a polymer contg. 37.6% C, 5.1% H, 21.47% Si, 8.84% Al and 1.49% Cl.

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Synthesis of methylethylethoxychlorosilane and determination of its thermal stability. organosilicon

X.A.Andrianov, S.A.Golubtsov and N.P.Lobusevich. Zhur.Obshchei Khim.27, 918-20(1957).

To 40.6 g. Mg at 40° was added in 3-4 hrs. 265 g. $MeSi(OEt)Cl_2$, 107 g. EtCl and 250 g. Et_2O; after 3 hrs. at 50° the mixture was distd. yielding a range of fractions from which was isolated 31.5% $MeEtSi(OEt)Cl$, b_{752} 118-9°, n_D^{20} 1.4135, d_{20} 1.062, and 13% $MeSi(OEt)Cl_2$, b.96-9°. Similar reaction of $MeSi(OEt)_2Cl$ gave 52.4% $MeEtSi(OEt)_2$, b_{754} 134-5°, 1.3925, 0.8440. Refluxing 68 g. $MeEtSi(OEt)Cl$ in a fractionating column 50 hrs. gave 0.24% $MeEtSiCl_2$ (estd. from phys.constants of the 1st fraction). Similar treatment 50 hrs. at 100° gave 0.2% $MeEtSiCl_2$.

Alkoxysilanes. VII. Reaction of tetraacetoxysilane with alcohols. Synthesis of tetraalkoxy- and alkoxyacetoxysilanes. organosilicon

B.N.Dolgov, V.I.Davydova and M.G.Voronkov (Silicate Chem.Inst., Leningrad). Zhur.Obshchei Khim.27, 921-6(1957). Cf. this j.26,325(1956).

Addn. of ROH to $Si(OAc)_4$ at 50-70° gave after stirring at this temp. 1.5-2 hrs. a distillable material and undistillable residue of silicic acid gel. Thus, 54.2 g. $Si(OAc)_4$ and 68.4 g. BuOH gave 77% $Si(OBu)_4$, b_8 146.8°, d_{20} 0.8936, n_D^{20} 1.4181. Similarly were prepd.: 88% $(MeEtCHO)_4Si$, b_{10} 116.5-7.5°, 0.8880, 1.4078; 65% $(Me_3CO)_3SiOAc$, b_4 96.5-7°, if run at reflux, or 76% if run at 100°; attempts to prepare $(Me_3CO)_4Si$ failed. Also prepd.: 53% $Si(OEt)_4$; 80% $(PrO)_4Si$, b_{16} 115°, 0.9117, 1.4010; 77% $(iso\text{-}PrO)_4Si$, b_{17} 91-1.5°, 0.8772, 1.3945; 78% $(iso\text{-}BuO)_4Si$, b_{12} 129.5-30°, 0.8655, 1.4064; 87% $(C_8H_{17}O)_4Si$, b_3 253-5°, 0.9000, 1.4288; 81% $(PhO)_4Si$, m.48°. Distn. of 41.5 g. $(Me_3CO)Si(OAc)_3$ with 11 g. BuOH gave 50% $(Me_3CO)(BuO)Si(OAc)_2$, b_{12} 128-30°, n_D^{20} 1.4065, d_{20} 1.0140, also formed in 70% yield from 66 g. $Si(OAc)_4$ and 19 g. Me_3COH and 18 g. BuOH. Also reported are: $(Me_3CO)_2Si(OAc)_2$, b_2 102.5-2.5°, 1.4040, 1.0196, 47.5%;

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92% $(BuO)_2Si(OAc)_2$, b_{13} 144-6°, 1.4099, 1.0225; 85% $(sec\text{-}C_8H_{17}O)_3SiOAc$, b_3 198.7-9.7°, 1.4291, 0.9064. Reaction of $Si(OAc)_4$ with MeOH gave an azeotropic mixture of $(MeO)_4Si$ and AcOH. Reaction of 26.5 g. $Si(OAc)_4$ with 27.1 g. PrOH yielded a gel on heating to 95° and a high yield of AcOPr. The reaction of $Si(OAc)_4$ with PhOH is best run in C_6H_6 at 100°.

Direct synthesis of naphthyltrichlorosilane. organosilicon

P.S.Zamin and A.D.Petrov(Polytech. Inst., Gorkii). Zhur.Obshchei Khim. 27, 926-8(1957).

Reaction of 1-$C_{10}H_7Cl$ with Si-Cu was run in a 24x650 mm porcelain tube yielding with the usual Si-Cu alloy but 1-2% $RSiCl_3$ at even 600°. If 20% Ag_2O is added to the alloy the yield rises to 10-12%, yielding also 2-3% $SiCl_4$ and 10-15% $C_{10}H_8$. Thebest yield of $C_{10}H_7SiCl_3$ (I) was 25% when the Si-Cu alloy was mixed with 20% Ag_2O and dry HCl was passed through the tube during reaction at 500-540°; flow rate of 8-10 g./hr and finely particulated alloy are essential to this yield. The product, b_4 148°, readily gave $C_{10}H_7SiEt_3$ on treatment with EtMgBr; this product, b_3 132-3°, d_{20} 0.9734, n_D^{20} 1.5712. I shows abs. max. 312 and 319 mμ; since pure 1-isomer of I has a single band at 312 mμ, it is believed that I from the direct synthesis above is a mixture of 1-2-isomers.

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Synthesis and properties of trisubstituted derivatives of 1-naphthylsilane. P.S.Sanin (Polytech.Inst.,Gorkii). Zhur.Obshchei Khim.27, 1886-90(1957). To 1-$C_{10}H_7MgBr$ from 36.4 g. RBr was added 38 g. $SiCl_4$ and the mixture was allowed to stand overnight, was refluxed 0.5 hr. and treated with 1.5-fold excess of EtMgBr; after refluxing 2 hrs., the solvent was distd. and the residue heated 2 hrs. on a steam bath, yielding 30% Et_4Si, and [redacted] 14.5g. yieldx of 1-$C_{10}H_7SiEt_3$ $b_3$142-5°, and 5.5 g. yield of $(1\text{-}C_{10}H_7)_2SiEt_2$, $b_2$251-2°, d_{20}1.1100. Reaction of 765 g. $SiCl_3$ with RMgX from 624 g. 1-$C_{10}H_7MgBr$ for 10 days at 18° gave after filtration and fractionation 60% 1-$C_{10}H_7SiCl_3$, $b_3$134-5°, m.53°. To MeMgI from 14.4 g. Mg was added 14.5 g. 1-$C_{10}H_7Si(OEt)_3$ and after refluxing 0.5 hr. the Et_2O was distd. and replaced by iso-Am_2O and the mixture was heated 4 hrs. at 140-50°, yielding after the usual aq. treatment 70% 1-$C_{10}H_7SiMe_3$, $b_{2.5}$102-5°, d_{20}0.9821, n_D^{20}1.5800. Similar use of 4-moles EtMgBr gave 1-$C_{10}H_7SiEt_3$, $b_5$142-5°, d_{20}0.9812, n_D^{20}1.5728. To MeMgI from 4.3 g. Mg was added 15 g. 1-$C_{10}H_7SiCl_3$ and after refluxing 2 hrs., distg. the Et_2O and heating the residue on a steam bath 1.5 hrs. there was obtained 80% 1-$C_{10}H_7SiMe_3$, $b_{2.5}$102-3°; similarly was obtained 82% 1-$C_{10}H_7SiEt_3$, from 0.15 mole $MeSiCl_3$ and 0.54 mole EtMgBr. Similarly PrMgBr gave 70% 1-$C_{10}H_7SiPr_3$, [redacted] $b_4$164°, d_{20}0.9553, n_D^{20}1.5568; BuMgBr gave 76.5% 1-$C_{10}H_7SiBu_3$, $b_5$188°, 0.9368, 1.5452. To 10.8 g. Mg in 50 ml. Et_2O was added over 2 hrs. 15 g. 1-$C_{10}H_7SiCl_3$ in 45.8 g. CH_2:$CHCH_2Br$ in 100 ml. Et_2O and after refluxing 0.5 hr. and aq. treatment there was obtained 82.6% 1-$C_{10}H_7Si(CH_2CH{:}CH_2)_3$, $b_3$151°, 0.9956, 1.5958. To 26.1 g. 1-$C_{10}H_7SiCl_3$ in 23.7 g. pyridine and 40 ml. Et_2O was added at -35° 0.4 mole MeOH in Et_2O; after warming to room temp. and refluxing 15 min., the mixture was washed with H_2O yielding 84.5% 1-$C_{10}H_7Si(OMe)_3$, $b_{3.5}$139-40°, m.28°. Similarly were prepd.: 82.5% tri-ethoxy analog, $b_3$142-3°, d_{20}1.0580, n_D^{20} 1.5298; 81.6% tri-isopropoxy analog, $b_3$156-8°, 1.0090, 1.5180; 82.8% tri-butoxy analog, $b_3$186-7°, 0.9967, 1.5106; 80.6% tri-n-hexoxy analog, $b_3$212-3°, 0.9660, 1.5018; 80% tris(2-ethylhexoxy) analog, $b_3$246-7°, 0.9488, 1.4990; 81% tris-sec.octoxy analog, $b_3$235-6°, 0.9485, 1.4945; 80% tri-cyclohexoxy

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analog, b_3 242-5°, 1.0700, 1.5440; 80% triallyloxy analog, $b_{3.5}$ 169-70°, 1.0684, 1.5460; simialrly was prepd. 80% $PhSi(OCH_2CH{:}CH_2)_3$, b_3 115-6°, 1.0142, 1.4892. The temp. of the reaction was raised to 5-20° for the higher mol.wt. alcs.

organosilicon

Halogenation of aromatic silanes. IV. Preparation and properties of chloro- and bromo- derivatives of p-tolyltrichlorosilane.

G.V.Motsarev and A.Ya.Yakubovich. Zhur.Obshchei Khim.27,1518-30(1957).

Cf. this j.25,412(1955).

Chlorination of 20 g. $p\text{-}MeC_6H_4SiCl_3$ (I) and 0.1 g. $SbCl_3$ 1 hr.40 min. at 22-50° until 2.9 g. was gained gave 84.7% $MeClC_6H_3SiCl_3$ (II), b_{15} 130-7°; purer product, b_{15} 132-3°, d_{20}^{20} 1.3948. Heated with Br-H_2O in sealed tube it gave 73% $MeClBrC_6H_3$, which oxidized with $K_2Cr_2O_7$-H_2SO_4 to 81.4% 2-chloro-4-bromobenzoic acid, showing that the silane was mainly m-chloro-p-tolyl deriv. Further chlorination of I as above, finally at 65-70° until a 20 g.sample gained 6 g., gave $MeCl_2C_6H_2SiCl_3$, b_{15} 150-6°, b_{15} 151-4°, d_{20}^{20} 1.5126 (16.2 g.), probably a mixture of 3,5- and 3,6-dichloro derivs. Further chlorination until 8.8 g. gain was reached gave from a 20 g. sample of I 20.8 g. $Cl_3MeC_6HSiCl_3$, b_{15} 168-72°, m.44-7°, a probable isomer mixture. Attempt to induce deeper chlorination at 95-100° resulted in weight gain of but 10.4 g. and gave some pentachlorotoluene, m.218-9°, tetrachlorotoluene, m.100-10°, and trichloro derivs. of I, isolated in part as polysiloxanes after aq. treatment. Chlorination of 20 g. I without catalyst at 22-5° 15 hrs. gave no wt.gain; continuation at 95-8° 13 hrs. gave 4.8 g.II mixed with its Cl-chloromethyl analog; the mixture, b_{15} 130-5°, d_{20}^{20} 1.4130. Redistn. gave m-Cl-$p\text{-}ClCH_2C_6H_3SiCl_3$, 7 g., b_{15} 135-7°, d_{20}^{20} 1.4645 (with Br-H_2O this gave after oxidation with $K_2Cr_2O_7$ 2-chloro-4-bromobenzoic acid). Addn. of 17.5 g. Br_2 to 22.2 g.I and 0.1 g. powd.Fe and heating finally 20 min. to 80° gave 30.2% $m\text{-}BrC_6H_3Me(\text{-}p)SiCl_3$, b_{10} 136-7°, d_{20}^{20} 1.6520, which solwly crystallized; with Br-H_2O it gave a dibromotoluene, b.256-40°, which oxidized to 2,4-di-

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bromobenzoic acid, m.171-3°. Similar bromination of I but with double proportion of Br_2 gave 28.1 g. di-bromo-I, b_{10} 163-6°, m.56-65°, which treat with Br-H_2O followed by oxidation , indicated the presence of various isomers, probably 3,5- and 3,6-dibromo-I. Attempt to induce deeper bromination with more Br_2 and higher reaction temp. (90°) gave $SiCl_3Br$ and mixed tetra-and-pentabromotoluenes, along with some tribromotoluenes. An aq. treatment of the residues gave a polysiloxane based on dibromo-I. When 13.6 g. Br_2 was added in 1.5 hrs. to 19.2 g. I and the mixture was heated 12.5 hrs. at 90-5° there was obtained 16 g. p,m-$(BrCH_2)C_6H_3BrSiCl_3$, b_{10} 148-50°, d_{20}^{20} 1.6553, confirmed by treatment with Br-H_2O, followed by oxidation.

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Synthesis of alkylchlorosiloxanes by the method of heterofunctional condensation.

N.N.Sokolov and K.A.Andrianov (V.I.Lenin AllUnion Electrotech.Inst.,Moscow).

Izvest.Akad.Nauk S.S.S.R.1957, 806-11.

Condensation between silanes contg. EtO and Cl groups proceeds stepwise and is a convenient route to low mol.wt. polysiloxanes. To 360 g. Me_2SiCl_2 was added 128 g. EtOH and after heating at 80° to complete the reaction, there was obtained 65.5% $Me_2Si(OEt)Cl$, b_{745} 94-5°. This was allowed to react with various chlorosilanes in the presence of 0.5% $FeCl_3$ at 48-60° and the filtered mixtures were fractionated. Equimolar mixture of Me_2SiCl_2 and $Me_2Si(OEt)Cl$ gave: 28% $(Me_2SiCl)_2O$, b_{738} 135.5°, 16% $Me_2SiClOSiMe_2OSiMe_2Cl$, b_{738} 178°, and 10% $Me_2SiClOSiMe_2OSiMe_2OSiMe_2Cl$, b_{738} 216°. Reaction of 1:1 ratio of $Me_2Si(OEt)Cl$ with Et_2SiCl_2 results in reaction of but 1/3 of the amount of the 2nd substance, yielding mainly products with 4-5 Si atoms per molecule; reaction of 2 moles Et_2SiCl_2 to 1 mole $Me_2Si(OEt)Cl$ gave: 14% $Et_2SiClOSiMe_2Cl$, b_{18} 77°, m. -107°, d_{20}^{20} 1.0299, 13.7% $Et_2SiClOSiMe_2OSiMe_2Cl$, b_{18} 106°, m. -103°, d_{20}^{20} 1.0197, and 5% $Et_2SiClOSiMe_2OSiMe_2OSiMe_2Cl$, b_{18} 130-3°, m. -95°, d_{20}^{20} 1.0158. Reaction of 2 moles $MeSiHCl_2$ and 1 mole $Me_2Si(OEt)Cl$ gave 18.3% $MeSiHClOSiMeHCl$, b_{747} 103°, m. -128°, d_{20}^{20} 1.0835, 10% $Me_2SiClOSiMeHCl$, b_{747} 120°, m. -120°, d_{20}^{20} 1.0609, 6.4% $MeSiHClOSiMeHOSiMeHCl$, b_{747} 148°, m. -112°, d_{20}^{20} 1.0585, and 2.2% $Me_2SiClOSiMeHOSiMeHCl$, b_{747} 159°, m. -111°, d_{20}^{20} 1.0515. $FeCl_3$ catalyzes the disproportionation of siloxanes which contain a Si-H link. Thus $EtSiHCl_2$ and $Me_2Si(OEt)Cl$ gave among other products: 7.7% $Me_2SiClOSiEtHCl$, b_{70} 74°, m. -110°, d_{20}^{20} 1.0519, 8.1% $EtSiHClOSiEtHCl$, b_{70} 81-2°, m. -128°, d_{20}^{20} 1.0609, 8.8% $Me_2SiClOSiEtHOSiEtHCl$, b_{12} 81.5-2°, m. -108°, d_{20}^{20} 1.0355, and 3.3% $EtSiHClOSiEtHOSiEtHCl$, b_{12} 89-90°, m. -111°, d_{20}^{20} 1.0453. Chlorination of the siloxanes at 11-38° (cf. Andrianov et al. Zhur.Obsh.Khim.26,933(1956)) gave: $MeSiCl_2OSiMeCl_2$, 88%, b_{750} 141°, m. -22°, d_{20}^{20} 1.5081; 82% $Me_2SiClOSiMeCl_2$, b_{750} 151°, m.-29°, d_{20}^{20} 1.1803; 73% $Me_2SiClOSiEtCl_2$, b_{750} 56°, m.-85°, d_{20}^{20} 1.2233; 66% $EtSiCl_2OSiEtCl_2$, b_8 94°, m.-60°, d_{20}^{20} 1.4009; 75% $Me_2SiClOSiEtClOSiMeCl_2$, b_{750} 110°,

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m.-56°, d_{20}^{20} 1.3290, and 80% $EtSiCl_2OSiEtClOSiEtCl_2$, b_3 110°, m.-36°, d_{20}^{20} 1.4626.

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Synthesis of α-trimethylsilylstyrene, 1-trimethylsilylcyclohexene and other unsaturated organosilicon compounds.

A.D.Petrov, V.F.Mironov and V.G.Glukhovtsev (Inst.Org.Chem., Acad.Sci. Moscow). Zhur.Obshchei Khim.27, 1535-9(1957).Cf. Izvest.Akad.Nauk SSSR, otdel.khim.nauk 1956,461.

To 23 g. Na in finely divided state under Et_2O there was added 50 g. Me_3SiCl, 5 ml. 1-chlorocyclohexene and 2 ml. EtOAc; after a reaction had commenced, 60 g. 1-chlorocyclohexene was added over 2 hrs., yielding 50 g. 1-trimethylsilylcyclohexene, b_{752} 171.5°, n^{20}_D 1.4628, d_{20} 0.8351, whose Raman spectrum was (cm^{-1}): 215(4), 266(1), 293(2), 321(0), 355(2), 381(0), 402(0), 439(1), 491(1), 539(3), 632(5), 660(0), 694(3), 729(0), 753(1), 837(3), 855(2), 911(2), 943(1), 970(1), 1000(1), 1039(2), 1079(2), 1124(0), 1179(2), 1195(1), 1251(1), 1271(3), 1308(2), 1354(2), 1377(1), 1409(1), 1435(4), 1448(1), 1460(1), 1620(4), 1575(0), 1653(0), 2833(4), 2865(3), 2900(10), 2933(2), 2957(9), 3005(2), 3032(1). Similarly, to 23 g. powd.Na in Et_2O was added 60 g. Me_3SiCl followed over 40 min. by 69 g. $PhCCl:CH_2$; after 2 days there was obtained 32 g. $Me_3SiCPh:CH_2$, b_3 52°, 1.5115, 0.8866. To Grignard reagent from 6.3 g. Mg and 57 g. $PhCH:CHBr$ was added 30 g. $PrMe_2SiCl$ and after distn. of Et_2O the residue was heated on a steam bath 6 hrs., then treated with H_2O, to yield 12 g. $PrMe_2SiCH:CHPh$, b_{18} 133°, 1.5218, 0.8908. To 250 g. abs.MeOH, 70 g. pyridine and 250 ml. C_6H_6 was slowly added 33 g. $(:CHSiCl_3)_2$ and after 2 days the mixture yielded 22.5 g. $(:CHSi(OMe)_3)_2$, b_2 80°, b_{743} 228-9°, 1.4155, 1.0782. Similar reaction of $CH_2:CHCl3SiCl_3$ gave 50% $CH_2:CHSi(OMe)_2Cl$, b_{743} 157.4°, 1.4183, 1.1109. Use of EtOH similarly gave $CH_2:CHSi(OEt)_3Cl$, b_{753} 184° (some decompn.), 1.4161, 1.0145. Similarly ClCH:$CHSiCl_3$ gave 41% $(MeO)_3SiCH:CHCl$, b_{746} 164°, 1.4195, 1.1097. Similarly $EtMe_2SiCl$ and 1-chloro-2-butyn-4-ol gave $Me_2EtSiOCH_2C:CCH_2Cl$, b_2 58°, 1.4593, 0.9965; similarly was prepd. 45% $Me_3SiOCH_2C:CCH_2Cl$, b_6 71°, 1.4538, 0.9988. To 46 g. powd.Na in MePh was added 3 ml. EtOAc followed by 78.5 g. Et_2SiCl_2 at 50°; after refluxing 2 hrs. and standing overnight the mixture yielded a range of products with mol.wts.

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up to 1200 and b_4 above 240°. Reaction of 10 g. $Me_3SiCH_2CH{:}CH_2$ and 48 g. MeCOSH [illegible] allowed by stand overnight gave spontaneously 14.5 g. $Me_3SiCH_2CHMeSCOMe$, b_{30} 126-7°, 1.4652, 0.9198. Equimolar mixture of $(MeO)_2PS_2H$ and $MePhSi(CH_2CH{:}CH_2)_2$ gave 90% $MePhSi[CH_2CHMeSP(S)(OMe)_2]_2$, n_D^{20} 1.5550, d_{20} 1.1799. Me_2SiCl_2 (450 g.) and BuMgBr from 500 g. BuBr gave 47.5% $BuMe_2SiCl$, b_{747} 138.4°, 1.4205, 0.8751; similarly were prepd.: 37.5% $PrMe_2SiCl$, b_{733} 113.8°, 1.4138, 0.8726, and $PrEt_2SiCl$, 21.2%, b_{739} 166.4°, 1.4347, 0.9024. To BuMgBr from 262 g. BuBr was added 65 g. $CH_2{:}CHSiCl_3$ and after 5 hrs. refluxing the mixture was treated with H_2O yielding 78.9% $Bu_3SiCH{:}CH_2$, b_{16} 128°, b_{13} 123°, 1.4494, 0.7988; similarly were obtained 65% $Me_3SiCH{:}CH_2$, b_{744} 54.6°, 1.3910, 0.6903; 67% $Et_3SiCH{:}CH_2$, b_{750} 146.5°, 1.4345, 0.7728; and 51.5% $Pr_3SiCH{:}CH_2$, $b_{750.5}$ 198.2°, 1.4430, 0.7852.

Alkoxysilanes. VIII. Alkyl(aryl)acetoxysilanes and their reaction with aliphatic alcohols.

organosilicon

S.N.Dolgov, V.F.Davydova and M.G.Voronkov (Silicate Chem. Inst., Leningrad). Zhur.Obshchei Khim.27, 1533-9(1957). Cf. this J.27,921(1957).

Distn. of a mixture of 163.5 g. $PhSiCl_3$ and 260.2 g. Ac_2O after standing 10-20 hrs. gave 33.5% $PhSi(OAc)_3$, b_1 153°, d_{20} 1.1939, n_D^{20} 1.4708; on chilling the product solidified and m.34.5°. Thus were prepd.: 70% $MeSi(OAc)_3$, b_3 87-8°, m.40.3°; 94% $Me_2Si(OAc)_2$, b_{750} 165°, 1.0540, 1.4030; 35% Me_3SiOAc, b_{760} 103-4°, 0.3914, 1.3875; 70% $EtSi(OAc)_3$, b_8 107.5-8.5°, 1.1428, 1.4123; 90% $Et_2Si(OAc)_2$, b_5 73.3°, 1.0240, 1.4152; 74.5% $BuSi(OAc)_3$, b_4 112-4°, 1.0872, 1.4155; 78% iso-$BuSi(OAc)_3$, b_4 101-2°, 1.0964, 1.4158; 81% $MeEtCHSi(OAc)_3$, b_7 116-7°, 1.0988, 1.4185; 70% $C_6H_{11}Si(OAc)_3$, b_2 121-2°, 1.1367, 1.4430. Refluxing 30 g. Me_2SiCl_2 in 70 ml. C_6H_6 through a Sohxlet thimble with 30 g. dry NaOAc 3 hrs. gave 76% $Me_2Si(OAc)_2$, b_{750} 165°; the reaction with Ac_2O as above gave a 90% yield. To 28.5 g. $MeSi(OAc)_3$ was added 23.5 g. PrOH giving an exothermic reaction; after stirring with cooling 1 hr. the

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mixture yielded 79% $MeSi(OPr)_3$, b_{14} 85.5-6.5°, b_{13} 85.5°, 0.8831, 1.3990, if the mixture was directly distilled in vacuo. Thus were prepd.: 79% $MeSi(OPr)_3$ above; 47% $(iso\text{-}BuO)_3SiMe$, b_{18} 101.5°, 0.8690, 1.4048; 84% $(C_6H_{13}CHMeO)_3SiMe$, b_2 201-2°, 0.8607, 1.4310; 84% $EtSi(OBu)_3$, b_{12} 138°, 0.8787, 1.4145; and 42% $PhSi(OBu)_3$, b_7 165-7°, 0.9450, 1.4608. If the reaction mixture is distd. at atm. pressure the acetoxysilanes react with the evolved ROH and the products are silanols and esters of AcOH; the silanols condense in the process to polysiloxanes. Reaction of 27 g. $PhSi(OAc)_3$ with 25 g. BuOH completed by 1 hr. at 100-20° gave 42% $PhSi(OBu)_3$. The reaction of acetoxysilanes with ROH requires heating if R is a tertiary radical. Thus the reaction of $MeSi(OAc)_3$ with Me_3COH in various proportions heated 3-28 hrs. at 120-30° gave up to 76.3% $MeSi(OAc)(OCMe_3)_2$, b_5 71.5°, 0.9431, 1.4020. Slow addn. of 26.4 g. Me_3COH to 78.5 g. $MeSi(OAc)_3$ and stirring 1 hr. gave after distn. in vacuo 55 g. $MeSi(OCMe_3)(OAc)_2$, b_{10} 91°, 1.0380, 1.4045. Thus were obtained: 63% $Me_2Si(OCMe_3)OAc$, b_{757} 155.6°, 0.9318, 1.3995; 64% $PhSi(OCMe_3)_2OAc$, b_3 137-9°, 1.0044, 1.4611; 52% $MeSi(OCMe_2Et)_2OAc$, b_1 92-4°, 0.9221, 1.4130; 40% $MeSi(OAc)(OCH_2CH_2CHMe_2)_2$, b_9 118-9°, 0.9273, 1.4131; 85% $MeSi(OAc)_2OCH_2CH_2CHMe_2$, b_{11} 108-9°, 1.0333, 1.4085; 20% $(C_6H_{13}CHMeO)_2SiMeOAc$, b_1 150-1°, 0.9151, 1.4250; 40% $(C_6H_{13}CHMeO)SiMe(OAc)_2$, b_1 115-6°, 0.9879, 1.4170; 77% $Me_2Si(OBu)OAc$, b_3 44.5-6°, 0.9203, 1.4021.

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organic boron

Esters of boric acid in the Friedel-Crafts reaction.

V.K.Kuskov, B.M.Sheiman and Z.I.Maksimova (State Univ.,Moscow). Zhur. Obshchei Khim.27, 1454-9(1957).

Esters of boric acid can be used in the Friedel-Crafts form of alkylation of aromatic compounds, such as C_6H_6, MePh, m-xylene, PhCl and PhOH. The mixture of $(RO)_3B$ and the aromatic compound is treated at 20-5° with $AlCl_3$ and the mixture heated 0.5-14 hrs. at 45-100° depending on the reactivity of the substrate. Yields of the alkylated products range up to 80-2%, although mainly 40-65% yields are obtained. The esters used included $(EtO)_3B$, $(PrO)_3B$, $(BuO)_3B$, $(iso\text{-}BuO)_3B$, $(iso\text{-}AmO)_3B$, tris-2-ethylhexyl borates, $(C_8H_{17}O)_3B$, $(C_6H_{11}O)_3B$, $(PhCH_2O)_3B$, $(CH_2{:}CHCH_2O)_3B$, $(ClCH_2CH_2O)_3B$ and ethylene glycol borate. The esters were prepd. by azeotropic dehydration of ROH and $B(OH)_3$ in C_6H_6 with anhydrous $CuSO_4$. Thus were reported: 36% $(EtO)_3B$, b.117-20°, d_{20} 0.8660, n_D^{20} 1.3775, and tris-2-ethylhexyl borate, b_3 183-5°, 0.8619, 1.4585. Heating 9.4 g. $(PrO)_3B$ with 9 g. $AlCl_3$ in 65 ml. $PhNO_2$ 3.5 hrs. at 60-75° gave no HCl nor PrCl. While predominantly p-isomers of alkylated products were obtained, the normally expected o-derivs. were also found. Prolonged reaction of C_6H_6 with 3 moles $AlCl_3$ and 1 mole $(EtO)_3Al$ gave 47.2% EtPh and 4.6% $Et_2C_6H_4$; $(MeO)_3Al$ or $(PrO)_3Al$ failed to react.

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organic

Reaction of cyclopropane hydrocarbons with mercuric salts.

VI. Organomercury compounds from phenylcyclopropane.

R.Ya.Levina, V.N.Kostin and V.A.Tartakovskii (State Univ., Moscow).

Zhur.Obshchei Khim.27, 881-5(1957). Cf. this J.26,2998(1956).

Shaking 122 g. $Hg(OAc)_2$ with 45 g. $PhCHCH_2CH_2$ in 430 ml. H_2O 12 hrs. gave after extn. with Et_2O, and distn. of the ext. 71% $PhCH(OH)CH_2CH_2HgOAc$, m.65-6°; this in ice cooled aq. soln. was treated with KBr, KI, KCNS and KCN. but only $PhCH(OH)CH_2CH_2HgCNS$, m.61°, was isolated. Treatment of the acetate with Na stannite gave $Hg(CH_2CH_2CH(OH)Ph)_2$, m. 77-8°(from aq. Me_2CO). Shaking 27 g. $Hg(OAc)_2$ and 10 g. $PhCHCH_2CH_2$ in dry MeOH 12 hrs. gave 82% $PhCH(OMe)CH_2CH_2HgOAc$, an oil. This with appropriate K salts gave: $PhCH(OMe)CH_2CH_2HgCl$, m.82°, $PhCH(OMe)CH_2CH_2HgBr$, m.87°; $PhCH(OMe)CH_2CH_2HgI$, m.79°; $PhCH(OMe)CH_2CH_2HgCN$, m.84°. To EtMgBr from 3.9 g. Mg was added dropwise 30 g. $PhCH(OH)CH_2CH_2HgCl$ in Et_2O; after refluxing 1 hr. and decompn. with aq. AcOH there was obtained $EtHgCH_2CH_2CHPhOH$, an oil, which heated in vacuo symmetrized and yielded 51% Et_2Hg and 47.5% $Hg(CH_2CH_2CH(OH)Ph)_2$. When 3 moles of EtMgBr was used per mole of Hg deriv. and the mixture was refluxed 12 hrs. there were obtained: Et_2Hg, 46% EtPhCHOH, which was identified through 3,5-dinitrobenzoate, m.67-8°.

and

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Synthesis of mixed organoarsenic compounds of type ArAr'AsX and ArAr'Ar"As from double diazonium salts.

A.N.Nesmeyanov, O.A.Reutov, Yu.G.Bundel and I.P.Beletskaya (M.V.Lomonosov State Univ.,Moscow). Izvest.Akad.Nauk S.S.S.R. 1957, 929-41.

To 10 g. $PhAsI_2$ in Me_2CO was added at 0° 6.7 g. $PhN_2Cl.ZnCl_2$ and the mixture, after evolution of N_2 had subsided, was filtered, the ppt. washed with Me_2CO, and filtrates evapd., gave a viscous liquid which after washing with 1:1 HCl and treatment with 40% KOH gave $(Ph_2As)_2O$, m.91%, in 71% yield. To 9.6 g. $PhN_2Cl.ZnCl_2$ in Me_2CO was added 8 g. $PhAsCl_2$, followed at 0° by 9.0 g. NaI added over 1.5 hrs.; after treatment as above there was isolated 42% $(Ph_2As)_2O$. Similarly was prepd. 39%$(p\text{-}ClC_6H_4AsPh)_2O$, which with HCl gave $p\text{-}ClC_6H_4AsPhCl$, $b_6$180-90°; oxidation of this with 30% H_2O_2 gave $p\text{-}ClC_6H_4AsPhO_2H$, m.161-2°. Similarly $p\text{-}O_2NC_6H_4N_2Cl.FeCl_3$, $PhAsCl_2$ and NaI gave p-$O_2NC_6H_4AsO_3H_2$, dec.300°, and 51.6% $(p\text{-}O_2NC_6H_4AsPh)_2O$, which with HCl gave the chloroarsine, $p\text{-}O_2NC_6H_4AsPhCl$, $b_6$170-90°, which with H_2O_2 gave $p\text{-}O_2NC_6H_4AsPhO_2H$, m.173°. Similarly was obtained $o\text{-}O_2NC_6H_4AsPhO_2H$, m.193.5°, through the oxide $(o\text{-}O_2NC_6H_4AsPh)_2O$. Similarly was prepd. 80% $o\text{-}MeO_2CC_6H_4AsPhO_2H$, dec.above 300°, and 50% $o\text{-}HO_2CC_6H_4AsPhO_2H$, m. above 300° (intermediate $o\text{-}HO_2CC_6H_4AsPh)_2O$ formed in 50% yield with some 20% Me ester. Similarly $PhAsCl_2$ and $o\text{-}EtOC_6H_4N_2Cl.FeCl_3$ and NaI gave 64% $(o\text{-}EtOC_6H_4AsPh)_2O$, which oxidized with H_2O_2 to $o\text{-}EtOC_6H_4AsPhO_2H$, m.182°. Analogously was obtained 63%$(2\text{-}C_{10}H_7AsPh)_2O$, which gave $2\text{-}C_{10}H_7AsPhO_2H$, m.157-9°; 71%$(p\text{-}MeC_6H_4AsPh)_2O$, which gave 37% $p\text{-}MeC_6H_4AsPhCl$, b_{18}190-225°, which gave $p\text{-}MeC_6H_4AsPhO_2H$, m.162°. RN_2Cl and $PhAsCl_2$ with NaI gave as above$(p\text{-}BrC_6H_4AsPh)_2O$, which gave $p\text{-}BrC_6H_4AsPhCl$, $b_6$178-90° for 25% overall yield, and this gave $p\text{-}BrC_6H_4AsPhO_2H$, m.176°. To 5.6 g. $p\text{-}MeC_6H_4N_2Cl.ZnCl_2$ in Me_2CO was added 5.7 g. $p\text{-}ClC_6H_4AsPhCl$ and at 0° over 50 min. was added 1.5 g. powd.Fe, yielding after aq. treatment 38% $(p\text{-}MeC_6H_4)(p\text{-}ClC_6H_4)AsPh$, viscous liquid; $HgCl_2$ adduct, m.188-9°. Use of $p\text{-}BrC_6H_4AsPhCl$ similarly gave 52% $(p\text{-}MeC_6H_4)(p\text{-}BrC_6H_4)AsPh$,

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$Me_2C{:}CHCHO$, 260 ml. Me_2CO, 500 ml. C_6H_6 and 87 g. 35% C_6H_6 soln. of $(t\text{-AmO})_3Al$ under N_2 40 hrs., followed by treatment with cold dil. H_2SO_4; the yield was 68% when $(iso\text{-PrO})_3Al$ was used.

Synthesis and chemical transformations of trichloromethyl and ω,ω-dichloroallyl derivatives of mercury. organomercury

A.N.Nesmeyanov, R.Kh.Freidlina and F.K.Velichko (Inst.Hetero-org.Compounds, Acad.Sci., Moscow). Doklady Akad.Nauk S.S.S.R.114, 557-9(1957).

Ultraviolet illumination of Hg and appropriate halogen compounds at 70-80° gave: 41% CCl_3HgBr, m.165°; $CHCl_2HgBr$, 1.2%, m.152°; $CHCl_2HgI$, 2.5%, m.130°; 67% $CCl_2{:}CHCH_2HgI$, m.46°; and 12% CCl_3HgI, m.117°. Reaction of CCl_3Br with theor. amount of 0.5% Na-Hg gave C_2Cl_6 and a little CCl_3HgBr. Neutralization of aq. soln. of CCl_3HgOH with HCl or HI gave CCl_3HgCl, m.173°, and CCl_3HgI; similarly $CCl_2{:}CHCH_2HgI$ gave $CCl_2{:}CHCH_2HgCl$, m.100°, and $CCl_2{:}CHCH_2HgBr$, m.94.5°. Heating RHgI with $HgCl_2$ in Et_2O or EtOH readily gives RHgCl. Exchange reaction with NaI and $CCl_2{:}CHCH_2Cl$ gave $CCl_2{:}CHCH_2I$, b_{10} 69-70°. CCl_3HgCl and NH_3 in $CHCl_3$ gave 95.5% infusible $ClHgNH_2$. Reaction of CCl_3HgBr in EtOH with H_2S instantly gave HgS. CCl_3HgBr and PhMgBr gave $PhHgCCl_3$ and PhHgBr. CCl_3HgBr and Ph_2SnCl_2 gave 49% $PhHgCCl_3$ when 3 moles of NaOH per mole of Hg deriv. was used; with larger amount of NaOH the reaction gave 29% Ph_2Hg; $PhHgCCl_3$ and MeOH-HCl gave PhHgCl in 100% yield. Heating $PhHgCCl_3$ in sealed ampul 0.5 hr. at 150° gave 80% PhHgCl. Photochemical treatment at room temp. of $PhHgO_2CCl_3$ in MeOH gave only PhHgCl and starting material; the result was the same on heating the compound to 240°. CCl_3HgX does not yield the R_2Hg analogs on treatment with KI, Cu or $Na_2S_2O_3$. Also cited are: $CCl_3HgBr.C_5H_5N$, m.87°; CCl_3HgOH, m.175°; $PhHgCCl_3$, m.116°; $PhHgO_2CCl_3$, m.240°; $CCl_2{:}CMeCH_2HgI$, m.101°; bromide, m.109°; chloride, m.127°.

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Derivatives of dimethylaminoazobenzene containing fluorine.

L.M.Yagupol'skii and M.S.Marenets. Zhur.Obshchei Khim.27, 1395-9(1957). Heating 1.8 g. p-AcNHC$_6$H$_4$SMe in AcOH with 6 ml. 30% H_2O_2 2 hrs. gave 71% corresponding sulfone, m.185-6°, which refluxed until dissolved in 8 ml. 15% HCl and treated with NaOH gave 83%n p-H_2NC$_6$H$_4$SO$_2$Me, m.134-35°. Addn. of 2.8 g. p-O_2NC$_6$H$_4$SeMe in EtOH to 15 g. $SnCl_2$ in 26 ml. concd.HCl at 60-70° gave after heating 1 hr. and treating with ice-NaOH p-H_2NC$_6$H$_4$SeMe, b$_5$103-5°; Ac deriv., m.99-100°. Azo coupling of appropriate amines with Me_2NPh gave the following p-Me_2NC$_6$H$_4$N:NC$_6$H$_4$R: p-MeS, 83%, m.175-6°, abs.max. 429 mμ; p-CF_3S, 80%, m.169-70°, abs.max. 432; p-MeSO$_2$, 60%, m.223-4°, abs.max. 445; p-CF_3SO_2, 82%, m.175-6°, abs.max. 476; p-CF_3O, 75%, m.131-2°, abs.max.419; p-CF_3, 75%, m.175°, abs.max. 430; p-MeSe, 80%, m.175-6°, abs.max.420; o-CF_3, 50%, m.120°, abs.max.425. Spectra in EtOH and in alc.HCl are discussed. The F-bearing derivs. show a shift of absorption to shorter wavelengths.

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Synthesis of some fluorine containing α-aryl-β-alanines. organic

V.P.Mamaev (D.I.Mendeleev Chem.Tech.Inst.,Moscow). Zhur. Obshchei Khim. 27, 1290-3(1957).

Refluxing 15 g. p-MeC_6H_4F, 24.9 g. $(CH_2CO)_2NBr$ and 0.9 g. Bz_2O_2 in CCl_4 2 hrs. gave 78% p-$BrCH_2C_6H_4F$, b_{10} 82°, which refluxing in $CHCl_3$ with urotropin gave 92% quaternary salt, which refluxed 2 hrs. with 50% AcOH gave 72% p-FC_6H_4CHO, b.177-8°. This (6 g.) refluxed with 5.1 g. $CH_2(CO_2H)_2$, 7.7 g. NH_4OAc and 10 ml. EtOH 4.5 hrs. gave 63% p-$FC_6H_4C(NH_2)HCH_2CO_2H$, dec.223°, and 15% more sol. p-$FC_6H_4CH{:}CHCO_2H$, m.206-7°. The amino acid gave N-benzoyl deriv., m.188-9°. Similar sequence of reactions starting with 3-fluoro-4-methoxytoluene gave 60% 3-fluoro-4-methoxybenzyl bromide, b_{25-8} 149-55°, m.39-41°, which gave 90% urotropin salt, which gave 55% 3-fluoro-4-methoxybenzaldehyde, b_5 105-6°, m.28-30°, which gave 58% 3,4-F(MeO)$C_6H_3C(NH_2)HCH_2CO_2H$, m.211-12°(from aq.EtOH), and 23% 3,4-F(MeO)$C_6H_3CH{:}CHCO_2H$, m.216-7°. This refluxed in aq.HBr 2 hrs. gave 70% m-fluoro-β-tyrosine HBr salt, which gave the free amino acid, dec.163.5-4°(from H_2O) as monohydrate; anhydrous acid, dec.169°. Treatment with BzCl gave O,N-dibenzoyl deriv., m.190.5-1.5°.

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Acetylati[illegible]kness, V.N.Filippova and I.F.Seits (Blood Transfusion Inst., Leningrad). Doklady Akad.Nauk S.S.S.R.114, 1076-9(1957). bio-radiology

Acetylating function of the coenzyme A system was tested on liver homogenates of pigeons using sulfanilamide (as well as p-aminobenzoic acid, hydroxylamine, p-aminoazobenzene, Na p-aminoazobenzene-p-'sulfonate and

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H acid) as substrate. Radiation sickness reduced the acetylating ability by a factor of about 3. The activity reduction is due to deficiencies in the protein component of the enzyme system as such, and not to mere deficiency of concn. of the enzyme, since large excess failed to bring about normal levels of acetylation. In the irradiated pigeons the content of the coenzyme is about 67 units per gram. of liver tissue. The birds received 2000-3000 r doses on X-radiation for the tests.

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organic C

Determination of activity of organic compounds containing radioactive carbon-14.

I.A.Korshunov, R.V.Amenitskaya and N.F.Novtorov(State Univ,Gorkii). Zhur.Obshchei Khim.27, 893-6(1957).

It was shown that direct detn. of C^{14} activity is possible in compounds such as AcOH, Me_2CO, EtOAc, $EtCO_2Et$, $PrCO_2Et$. The filling gas for the counter tube may be CO_2 or argon. The substances are handled in a vacuum train, the diagram of which is shown. Standard counting tubes with Cu cathode and W anode are used; these are sealed to the vacuum train and are enclosed in Pb shells. If the quenching ability of the org. substance is insufficient, some 10-20 EtOH may be introduced into the system. The accuracy of detns. is ± 2%.

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Organic radiology

Preparation of 2,3-dimercaptopropanol containing radioactive sulfur. A.N.Nesmeyanov, A.B.Silaev and V.M.Fedoseev (State Univ.,Moscow). Zhur. Obshchei Khim.27, 1280-2(1957).

The following method yields S^{35}-labeled BAL with high activity. $Na_2S^{35}.9H_2O$ was treated with 1:1 HCl, the resulting H_2S passing into EtONa soln., after which ordinary H_2S was used to saturate the residual EtONa; the soln. was kept in ampul with $BrCH_2CHBrCH_2OH$ 5 days and the operation was repeated with fresh NaSH soln. After 5 days more the mixture was acidified with HCl and the mixture was filtered and coned. in vacuo under N_2; after extn. with $CHCl_3$ there was obtained 57% S^{35}-labled $HSCH_2CH(SH)CH_2OH$, $b_{0.2}$ 64-5°, n_D^{20} 1.5730, d_{20} 1.2500. Isotope exchange between this and $NaS^{35}H$ was studied, in 80% EtOH. It was shown that at 87° no exchange occurs.

bio-organic

Conditions and mechanism of synthesis of phosphoryl choline containing P-32. A.B.Silaev, A.N.Nesmeyanov and V.M.Kutyurin(State Univ.,Moscow). Zhur. Obshchei Khim.27, 1283-6(1957).

Combustion of P^{32} (red form) gave labeled P_4O_{10} which was quenched in H_2O with heating to yield labled H_3PO_4. This (6.0979 g.) treated with 2.3593 g. choline chloride was heated to 100° at 1-2 mm. (these are optimum conditions) until HCl evolution ceased; the mass was then treated with 4.4385 g. P_4O_{10} and heated as above 30 hrs. After treatment with aq. NH_4OH, with boiling 1 h the phosphate ion was pptd. with magnesia mixture and the filtrate on treatment with $CaCl_2$ gave Ca salt of phosphoryl choline after addn. of EtOH. The incorporation of P^{32} occurs through both the P_4O_{10} and H_3PO_4 components of the reaction mixture; under 1-2 mm. vacuum both participate equally. No exchange of P^{32} occurs between phosphoryl choline and mono-salts of H_3PO_4 in neutral or acid media at 100°. This indicates very stable ester link.

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Association of organolithium compounds of aliphatic series in hydrocarbon solutions.

K.B.Pietrovskii and M.P.Remina (S.V.Lebedev Synthetic Rubber Res.Inst.). Doklady Akad.Nauk S.S.S.R.115, 757-9(1957).

Solns. of about 0.6N LiEt and 0.6-0.8N LiBu were examined cryoscopically in C_6H_6 and cyclohexane. It was shown that LiEt in C_6H_6 is associated to double mol.wt. LiBu is also associated similarly in C_6H_6. In cyclohexane the results for LiBu are also similarly indicative of strong dimerization.

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Organoboron compounds. 19. Synthesis of alkylboron dichlorides. B.M.Mikhailov and T.A.Shchegoleva (N.D.Zelinskii Inst.Org.Chem., Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1080-5. Cf. this J.1956, 508.

To 156 g. $B(OMe)_3$ in 400 ml. Et_2O was added at -75° over 9 hrs. EtMgBr from 36 g. Mg and on the following day (all operations under N_2) the mixture was treated with dil.HCl, the org.layer was freed of Et_2O and slowly distd. with BuOH until the temp. of distillate reached 115°, yielding 53% $EtB(OBu)_2$, $b_7$70-1°, d_{20}0.8224. Similarly was prepd. 50% iso-$PrB(OBu)_2$, $b_7$78-8.5°, d_{20}0.8187. Slow distn. of $EtB(OBu)_2$ and hexyl alc. gave 83.5% $EtB(OC_6H_{13})_2$, $b_9$130-1°, d_{20}0.8302[similarly was prepd. 80% $PrB(OC_6H_{13})_2$, $b_7$130-1°, d_{20}0.8283, and 72% iso-$PrB(OC_6H_{13})_2$, $b_6$125-6°, d_{20}0.8258. To 28.5 g. $EtB(OBu)_2$ was added over 1 hr. 31.8 g. PCl_5, yielding on distn. 78% $EtBCl(OBu)$, b_{30}49-52°, d_{20}0.9030, BuCl and $POCl_3$. Similar addn. to 32.2 g. $EtB(OC_6H_{13})_2$ of 55 g. PCl_5 and heating 0.5 hr. at reflux gave 50% $EtBCl_2$, b.49-51°, which ~~smgt~~ ignites in air and is easily hydrolyzed; the same formed in 40% yield from 17.5 g. $EtBCl(OBu)$ and 24.5 g. PCl_5. Reaction of 54 g. $EtB(OC_6H_{13})_2$ with 46.5 g. PCl_5 gave 3.4 g. $EtBCl_2$, 19.5 g. $EtBCl(OC_6H_{13})$, b_{10}63-5°, and 21% $EtB(OC_6H_{13})_2$. Reaction of 31.35 g. $PrB(OC_6H_{13})_2$ with 51.8 g. PCl_5 gave 73.5% $PrBCl_2$, b.73-5°, which also ignites in air. Similarly iso-$PrB(OC_6H_{13})_2$, (28.5 g.) and 46.7 g. PCl_5 gave 70% iso-$PrBCl_2$, b.70.5-3°, which ignites in air.

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Synthesis and transformations of unsaturated organosilicon compounds.
3. Synthesis of tertiary triatomic γ-silicon-bearing alcohols of the acetylenic series.

I.A.Shikhiev, M.F.Shostakovskii, B.V.Komarov and L.A.Kayutenko (N.D. Zelinskii Org.Chem.Inst., Akad.Sci.,Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1139-41. Cf. this j.1957,991.

To EtMgBr from 39 g. Mg there was added at -10° 50.4 g. $Me_2C(OH)C{:}CH$ and the mixture after being stirred 3 hrs. was left overnight, after which it was again stirred 2-3 hrs., treated with 1 g. Cr_2Cl_2 and 0.5 g. $MgCl_2$, and treated with strong cooling with 27 g. $SiCl_4$; after 12-15 hrs. of refluxing the mixture was treated with aq.HCl and extd. with Et_2O, yielding 53.4% $HSi[C{:}CCMe_2OH]_3$, m.163-3.5°(from dioxane). Similarly $Me_2C(OH)C{:}CH$ and EtMgBr with $MeSiCl_3$ gave 92% $MeSi(C{:}CCMe_2OH)_3$, m.214°, while the use of $CH_2{:}CHSiCl_3$ similarly resulted in 65.7% $CH_2{:}CHSi(C{:}CCMe_2OH)_3$, m.172.5-3°(from dioxane).

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Biochem

State of nerve elements in lymphadenous tissues in acute radiation disease. I.B.Soldatov (S.M.Kirov Milit.Med.Academy). Doklady Akad.Nauk S.S.S.R. 115, 803-5(1957).

Cats subjected to 700 r dose of X-radiation, with subsequent signs of the radiation sickness show dystrophic symptoms of necrosis in the lymphadenous tissues. Spleen, salivary glands and lymphatic nodes showed pathological changes in the nerve elements. The changes are illustrated photographically. The changes may adversely affect the various reflexes associated with these organs.

bio chem

Effect of X-rays on variability of Actinomyces subtropicus. S.I.Alikhanyan and F.S.Klepikova (All Union Antibiotics Res.Inst.). Doklady Akad.Nauk S.S.S.R. 115, 806-8(1957).

Treatment of the organism cultures, producers of albomycin, with X-ray doses up to 640,000 r was correlated with the production of antibiotic. Such irradiation tends to increase the diversity of activity in this respect, producing widely divergent plus and minus variants. The plus variants are unusual, the minus variants are common. Size of the dose is a factor and small or large doses may yield undesired results.

radiology

Role of earthworms in decontamination of soil from radioactive isotopes. A.A.Poredel'skii, N.A.Poryadkova, L.A.Rodionova and S.V.Tarchevskaya Doklady Akad.Nauk S.S.S.R. 115, 809-12(1957).

Earthworms kept in soil-sand boxes containing Co^{60} and planted with various grasses and other plants appear to improve the uptake of Co by the plant roots by several fold. The accumulation is best in younger plants. Thus earthworms facilitate the removal from the soil of Co^{60} which is normally strongly sorbed by the soil.

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Alkyl esters of ethylthioarsenious acid.

Gil'm Kamai and N.A.Chadaeva. Doklady Akad.Nauk S.S.S.R.115, 305-7(1957). Addn. of the appropriate amount of $EtAsCl_2$ to 2 moles RSH in a stream of dry CO_2, followed by gradual heating to 190-200° over 3 hrs. gave the following esters $EtAs(SR)_2$: diethyl, dipropyl, dibutyl and diisoamyl. Reaction of $EtAsCl_2$ with 2RSH in Et_2O in the presence of pyridine gave the diethyl, dibutyl and dihexyl esters; the latter are obtained in pure state if the filtrate from pyridine HCl salt is rapidly washed with ice water. The diethyl ester was also prepd. from $EtAsCl_2$ and 2EtSNa. Thus are reported $EtAs(SR)_2$ (R shown): Et, 30-41.9%, b_2 80-2°, $b_{1.5}$ 75-7°, d_{20} 1.2555 (from method 2, d_{20} 1.2593), n_D^{20} 1.5750; Pr, 40.3%, b_2 101-2°, 1.1906, 1.5565; Bu, 43.5-59.4%, b_2 122-3°, 1.1402(1.1374), 1.5442; iso-Am, 43.2%, b_2 135-6°, 1.0957, 1.5324; C_6H_{13}, 31.3%, $b_{1.5}$ 163-4°, 1.0778, 1.5280. The esters are gradually hydrolyzed by HgO in the cold, yielding $EtAsO_2H_2$ (by air oxidation). Keeping $EtAs(SBu)_2$ with MeI 13 days gave Me_2BuSI, m. 78-80°; reaction of $EtAs(SBu)_2$ with AcCl (5-18 hrs. at 150-60°) gave

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Reaction of cyclopropane hydrocarbons with salts of mercuric mercury. VII. Thermal decomposition of products of symmetrization of γ-mercurated alcohols. R.Ya.Levina, V.N.Kostin and V.A.Tartakovskii (State Univ., Moscow). Zhur. Obshchei Khim. 27, 2049-52(1957). Cf. this j. 26, 2998(1956), 27, 85(1957). Heating $(PhCH(OH)CH_2CH_2)_2Hg$ to 120-30° at 15 mm. gave a distillate of Hg and a mixture of EtPhCHOH and EtCOPh. Similar heating to 100-100 of $(Me_2C(OH)CH_2CH_2)_2Hg$ gave t-AmOH and Me_2CO, and Hg, with apparently 1-hexene. The 1st substance apparently yields free radicals the HO group of which is the source of H for the final products. The 2nd compound in its decompn. yields tertiary free radicals which are cleaved at the central C atom to yield the above products with probably intermediacy of Me_2CO, C_2H_4 and H_2.

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X-Ray studies of hetero-organic compounds. Stereochemistry of ferrocene and its derivatives.

Yu.T.Struchkov (Inst.Hetero-org.Compounds, Moscow). Zhur.Obshchei Khim. 27, 2039-49(1957). Cf. Dunitz et al., Nature, 171,121(1953).

Examn. of X-ray diffraction patterns of ferrocene and its derivs.: chloro, bromo, iodo, dichloro, dibromo, and diiodo, nitrophenyl, as well as bridged derivs. such as bis-ferrocenylmethane and bisferrocenylenephenylmethane, is generally reported. Structural detns. of diaxoferrocenes was reported elsewhere (cf. Doklady Akad.Nauk SSSR, 110,67(1956). Steric hindrance in ferrocene derivs. is discussed and the hindrance to ring rotation is shown. The most probable configurations are illustrated.

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organo metalo

α-Styryl compounds of lithium, mercury and thallium.

A.E.Borisov and I.B.Nevirova (Inst.Hetero-Org.Compounds, Acad.Sci.,Moscow).

Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1258-60.

Cf.Doklady Akad.Nauk SSSR 96, 289(1954).

Reaction of 0.76 g. Li in abs.Et_2O with 10 g. $PhCBr:CH_2$, which was added in 1.5 hrs. at 8-10° gave an Et_2O soln. of $PhCLi:CH_2$ (I). This with $HgBr_2$ gave after 1 hr. stirring and treatment with 1% HBr 33% $PhC(HgBr):CH_2$, m.89.5-90.5°(from Me_2CO), which with dry NH_3 in C_6H_6 gave in 1.5 hrs. 82% $(PhC:CH_2)_2Hg$, m.68-9°; the symmetrization is also effected by Na stannite in 84% yield. The product treated with $HgCl_2$ in Me_2CO gave 86% $PhC(HgCl):CH_2$, m.95-6°. The soln. of I, above, treated with $TlBr_3$ in Et_2O and the mixture decomposed with 1% HBr gave 22% $(PhC:CH_2)_2TlBr$ (II), m.156-8°, also formed from $TlBr_3$ and $(PhC:CH_2)_2Hg$ in Et_2O. Similarly $TlCl_3$ gave 70% $(PhC:CH_2)_2TlCl$, m.158-60°. II shaken with Hg in Me_2CO at 40° 5 hrs. gave 66% $(PhC:CH_2)_2Hg$.

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Reaction of halides of fluorinated carboxylic and thiocarboxylic acids with sodium azide.

Fluoro-organic

N.N.Yarovenko, S.P.Motornyi, L.I.Kirenskaya and A.S.Vasil'eva. Zhur.Obshche Khim.27, 2243-6(1957).

To 12 g. NaN_3 activated with $N_2H_4.H_2O$ was added at -5° 55.5 g. CF_3COBr without access of moisture in an app. with refrigerated condensers (-40°); after addn. of 400 ml. MePh the exit from the app. was connected to heated condensers (120°) for decompn. of CF_3CON_3 which is partly retained in the condensers, the exit from these passing into chilled traps, and the reactio mixture was heated gradually to 120° over 3.5 hrs. yielding a distillate of 44% CF_3NCO, b.-35°, which (4.5 g.) and 2.4 g. liq.HCl kept in sealed tub overnight gave 99% $CF_3NHCOCl$, n_D^{25}1.3545, d_{25}1.5551; similarly HBr gave 71.8 $CF_3NHCOBr$, n_D^{23}1.3869, d_{23}1.9489, which must be kept cold or under pressure; similarly liq.HF gave 71% CF_3NHCOF, n_D^{18}1.2970, d_{18}1.4907. CF_2ClCF_2SCl (36 g was added slowly to 80 g. Sn foil and 40 ml. 28% HCl at 40° yielding a

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$EtAsCl_2$ and AcSBu, b_{74} 89°, d_{20} 0.9441, n_D^{20} 1.4598. Similar reaction of $EtAs(SBu)_2$ with Ac_2O gave $EtAs(OAc)_2$ and AcSBu.

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a distillate of 15.6% $CF_2ClC(S)F$ (I), b.56°, d_4°1.5183, leaving a residue of 8.2 g. $(CF_2ClCF_2)_2S_2$, b.141°, n_D^{21}1.3915, d_4^{21}1.6810. I and NaN_3 allowed to react as described above gave 79% CF_2ClCN, b.-16°, the same being formed in 41% yield on heating $CF_2ClCONH_2$ with P_2O_5.

New methods of preparation of fluorinated carboxylic acids and esters of difluoromethyl alcohol. Fluoro-organic

N.N.Yarovenko, M.A.Raksha, V.N.Shemanina and A.S.Vasil'eva. Zhur. Obshchei Khim.27, 2246-50(1957).

To 44 g. Et_2NH in steel autoclave was added with liquid air cooling 40 g. $CF_2:CF_2$ and the mixture was warmed to room temp. 16 hrs.(max.pressure 18 atm.) after which it was treated with ice yielding 49% $CF_2HCONEt_2$ (I), b_{60}97°, n_D^{20}1.4155, d_{20}1.1180; if the original reaction mixture is carefully distd. there may be obtained the intermediate product, $CHF_2CF_2CEt_2$, b_{15}31°, which may be obtained in up to 80.5% yields. I (151 g.) and 40 g. NaOH in 400 ml. H_2O gave after evapn. 92% CHF_2CO_2Na, a solid, which distd. from H_2SO_4 gave 99% CHF_2CO_2H (II), b.134°, d_{20}1.530, n_D^{20}1.3419. The Na salt treated with PBr_3 and heated to 150° gave a distillate of 40% CHF_2COBr, b.48°, n_D^{20}1.3820, d_{20}1.8862. II (58 g.) in 58 ml.H_2O was treated with 65 g. HgO, kept 0.5 hr. filtered and concd. in vacuo yielding 91%$(CHF_2CO_2)_2Hg$, m.185°, dec.210°. This (19.5 g.) and 30 g. I_2 heated in small portions to 185° gave a distillate of 35% CHF_2I, b.22°, and 61.6% $CHF_2CO_3CHF_2$, b.64°, n_D^{20}1.300, d_{20} 1.5038, the latter also being prepd. from CHF_2I and the Hg salt above in sealed ampul overnight, in 93% yield. Passage of dry $CF_2:CFCl$ at 0° into Et_2NH and hydrolysis of the resulting mixture with H_2O gave $CHClFCONEt_2$ which heated with concd.H_2SO_4, distd.(b.140-65°), and treated with H_2SO_4, gave 59.5% $CHFClCO_2H$, b.162-4°, n_D^{20}1.4100.

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Organoboron compounds. 20. N-Substituted phenyldiaminoborons and B-phenylborazoles.

B.M.Mikhailov and P.M.Aronovich(N.D.Zelinskii Inst.Org.Chem.,Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1125-5. Cf. this j.1956,1144. To 41.4 g. $EtNH_2$ in C_6H_6 was added at -30° 31.8 g. $PhBCl_2$ in 30 ml. C_6H_6 and after warming to room temp. for 2 hrs. the mixture was filtered from $EtNH_2.HCl$ and evapd. yielding 3.5 g. B-triphenyl-N-triethylborazole, m.200-5°; the mother liquor from this gave $PhB(NHEt)_2$ (I), b_3 97-8°, d_{20} 0.924, n_D^{20} 1.5130, the latter is readily attacked by H_2O and atm. O_2. The residue after the distn. gave more triphenyltriethylborazole for a total yield of 21%, the pure substance, m.205-7°(from C_6H_6-petr.ether); the borazole is stable in air and is slowly attacked by hot alkaline H_2O_2. Heating I to 210° 2 hrs. gave 17.3% above triphenyltriethylborazole. Addn. of 12.7 g. $PhBCl_2$ to 29.3 g. $PhNH_2$ in C_6H_6 as above gave 54.7% $PhB(NHPh)_2$, m.83.5-5.5°(from hexane-isopentane), which is rapidly hydrolyzed by H_2O. Heating this to 270° gave $PhNH_2$ and 31.7% hexaphenylborazole, m. above 360°(from C_6H_5). $PhBCl_2$ and Et_2NH similarly gave 14.1% $PhB(NEt_2)_2$, $b_{0.2}$ 70-2°. All work was done under N_2.

21. New methods of synthesis of borazole derivatives.

B.M.Mikhailov and T.V.Kostrova. Ibid. 1128-7.

Reaction of 58 g. $p\text{-}MeC_6H_4B(OCH_2CHMe_2)_2$ with 48.6 g. PCl_5 gave 87.3% $p\text{-}MeC_6H_4BCl(OCH_2CHMe_2)$, b_8 113-5°, n_D^{20} 1.5017, d_{20} 0.9919. This (17.5 g.) treated with NH_3 in Et_2O gave after sepn. of NH_4Cl and evapn. 3.85 g. B-triphenylborazole, m.180-2°, and 79% $PhB(OCH_2CHMe_2)_2$, b_9 124-6°. Pure triphenylborazole, m.181-2.5°(from C_6H_6-isopentane); $PhBCl_2$ in C_6H_6 treated with NH_3 gave 96% above triphenylborazole, m.180-2°. Similarly were prepd. from the appropriate chloro esters: 85% B-tri-p-tolylborazole, m.189-90°; 84.9% tri-1-naphthylborazole, m.185-7°, while the use of appropriate amines gave: 72.6% B-triphenyl-N-triethylborazole, m.205-6°, and 46.8% B-tri-1-naphthyl-N-triethylborazole, m.269-71°.

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organosilicon

Alkoxysilanes. 9. 2-Fluoroethoxysilanes.

M.G.Voronkov and B.N.Dolgov (Silicate Chem.Inst.,Leningrad). Izvest.Akad. Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1128-9 (cf. Zhur.Obsh.Khim.27,1593(1957))

To 64.1 g. FCH_2CH_2OH and 38.1 g. $Si(OMe)_4$ was added 0.5 ml. $SiCl_4$ and the mixture was fractionated yielding MeOH and 70% $(FCH_2CH_2O)_4Si$, b_{766} 256°, d_{20} 1.2750, n_D^{20} 1.3991. To 0.5 g. K in 12.8 g. FCH_2CH_2OH was added 11.6 g. Et_3SiCl and after refluxing 3 hrs. during which 2.2 l. H_2 had evolved, there was obtained 80% $Et_3SiOCH_2CH_2F$, b_{764} 175.5°, 0.9068, 1.4129. The latter formed in 75% yield by transesterification of Et_3SiOMe by FCH_2CH_2OH as above.

organosilicon

Synthesis and transformations of oxygen-containing organosilicon compounds. 8. Reaction of vinyl ethers with silanes and β-silicon-bearing alcohols. I.A.Shikhiev, M.F.Shostakovskii and N.V.Komarov (N.D.Zelinskii Inst.Org. Chem.,Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1132-8 Cf. this j. 1956,1271.

To 24 g. $PhOCH{:}CH_2$ and 26.5 g. Et_3SiOH was added 2 drops concd.HCl and the mixture after 4 hrs. at 80° was kept overnight and neutralized with K_2CO_3 yielding 11.3 g. $(Me_3Si)_2O$, 7.4 g. PhOH and 28.7% $Et_3SiOCHMeOPh$, $b_{16.5}$ 130-1°; n_D^{20} 1.4795, d_{20} 0.9544. Similarly $BuOCH{:}CH_2$ and $EtMe_2SiCH_2CH(OH)CH{:}CH_2$ gave 80.6% $CH_2{:}CHCH(CH_2SiMe_2Et)OCHMeOBu$, b_3 98-8°, 1.4371, 0.8536.

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Synthesis and properties of some bis(trimethylsilyl)propylenes.

A.D.Petrov, V.F.Mironov, V.G.Glukhovtsev and Yu.P.Egorov (N.D.Zelinskii Inst. Org.Chem., Acad.Sci.,Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1091-1100. Cf. this j.1956,550.

Slow distn. up to 200° of 116 g. $Cl_2CHCH_2SiCl_3$ and 73 g. quinoline, filtration of the distillate and its redistn. gave 8 ml. $SiCl_4$ and 24 g. $Cl_3SiCH_2CHClCH_2Cl$, b_{748} 185°, n_D^{20} 1.4780, d_{20} 1.3880 (Raman spectrum, cm^{-1}: 156(2), 170(4), 192(6), 215(0), 242(1), 264(3), 301(6), 348(10), 423(0), 460(0), 503 (10), 524(0), 588(2), 705(1), 736(2), 771(2), 800(3), 829(2), 1510(2), 1530 (2), 1581(2), 1616(0), 1670(4), 1606(4), 2864(2), 2921(5), 2960(1), 3071(3)). The same formed from $Cl_3SiCH_2CHClCH_2Cl$ on being heated with quinoline. Thus, $Cl_3SiCH(CH_2Cl)_2$ and quinoline also gave 36.5% $Cl_3SiC(CH_2Cl)=CH_2$, b_{750} 164°, 1.4794, 1.3967 (Raman spectrum: 121(3), 150(2), 195(8), 225(3), 240(0), 296 (4), 360(7), 400(2), 430(1), 455(10), 505(3), 648(2), 695(2), 762(6), 799(0), 926(2), 954(1), 1116(0), 1145(1), 1274(1), 1502(1), 1425(3), 1610(3), 2944(2), 2965(4), 2994(2), 3050(3), 3085(4)). To $MeMgCl$ from 25 g. Mg was added 51 g. $Cl_3SiCH_2CHClCl$ and after usual treatment there was obtained 65% $Me_3SiCH_2CHClCl$ (I), b.157.5°, 1.4500, 0.9045. To 10 g. powd.Na in Et_2O was added 20 g. Me_3SiCl, 1 ml. EtOAc and a little I, and after the initiation of the reaction, 22 g.I was gradually added, yielding after 5 hrs. refluxing 60% $Me_3SiCH:CHSiMe_3$, b.165.5°, 1.4436, 0.7809(Raman spectrum: 127(3), 223(3), 244(2), 255(1), 310 (2), 377(2), 511(0), 550(2), 562(3), 619(10), 646(1), 695(3), 714(1), 757(0), 748(0), 774(4), 805(2), 845(1), 857(1), 965(1), 982(0), 1060(0), 1255(3), 1296(4), 1360(2), 1415(3), 1455(3), 1565(4), 2850(3), 2901(10), 2962(10), 3015(0). I Raman spectrum was: 204(3), 228(4), 245(1), 278(1), 300(3), 366 (3), 462(3), 527(3), 562(3), 597(1), 620(10), 646(2), 697(4), 750(3), 777(3), 804(2), 842(3), 872(0)(??? abstracter), 1259(3), 1300(4), 1376(3), 1416(3), 1448(1), 1560(1), 1590(1), 2852(3), 2903(10), 2965(10), 3071(3). Heating 308 g. $Cl_3SiCH_2CHClMe$ and 230 g. quinoline gave 49.5% $Cl_3SiCH:CHMe$ ($PhNEt_2$ does not act satisfactorily in this instance), b_{755} 135.5°, 1.4510, 1.3513;

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this percolated with Cl_2 18 hrs. gave 94% $Cl_3SiCHClCHClMe$, b_{740} 194°, b_{742} 196°, 1.4868, 1.4720 (Raman spectrum: 170(8), 185(5), 208(4), 232(2), 252(5), 307(8), 317(2), 387(1), 566(5), 590(8), 419(2), 438(2), 482(6), 498(5), 537 (5), 590(5), 606(5), 675(4), 700(1), 717(1), 755(2), 780(2), 808(1), 815(4), 848(0), 892(5), 929(1), 965(0), 1010(1), 1054(1), 1108(1), 1118(5), 1165(5), 1219(1), 1235(1), 1261(1), 1322(0), 1388(0), 1446(5), 1457(8), 2867(1), 2909 (1), 2940(5), 2994(5). This heated with quinoline gave 53% $Cl_3SiCCl{:}CHMe$, b_{739} 161.5°, b_{729} 159.5°, 1.4720, 1.3871, which with MeMgCl gave 96.5% Me_3Si-$CCl{:}CHMe$, b_{775} 135.2°, 1.4450, 0.8969 (Raman spectrum: 207(6), 250(1), 277(4), 337(1), 398(8), 497(0), 562(9), 631(10), 698(7), 760(5), 791(0), 811(0), 845(2), 888(2), 990(2), 1028(1), 1139(5), 1195(5), 1256(2), 1377(6), 1388(1), 1380(5), 1412(5), 1447(5), 1620(10), 2845(1), 2909(10), 2962(10), 3010(5)). Slow distn. of 125 g. $Cl_3SiCHClCHClMe$ and 1 g. $AlCl_3$ gave 62% mixed Cl_3Si-$CCl{:}CHMe$ and $Cl_3SiCMe{:}CHCl$, b_{748} 155°, 1.4600, 1.3845, which with MeMgCl gave 69% $Me_3SiCCl{:}CHMe$ and $Me_3SiCMe{:}CHCl$, b_{745} 152°, 1.4454, 0.8924, the identity of the components being shown by Raman spectrum containing lines 397(8), 560(9), 650(10), 697(7), and 1388(5) cm^{-1}. To 20 g. Na and 40 g. Me_3SiCl in Et_2O was added 48 g. $Me_3SiCCl{:}CHMe$ followed by several portions of 3-5 ml. EtOAc, yielding after prolonged heating 19.7 g. $(Me_3Si)_2C{:}CHMe$, b_{727} 175°, 1.4530, 0.8047 (Raman spectrum, 161(5), 200(5), 228(4), 261(4), 298(6), 304(7), 389(2), 430(1), 647(10), 689(6), 740(1), 770(2), 845(5), 888(2), 1035(2), 1250 (4), 1267(5), 1355(4), 1372(2), 1414(4), 1445(5), 1572(5), 2850(5), 2898(10), 2954(10), 2972(8)). Passage of Cl_2 into $Cl_3SiCH_2CH{:}CH_2$ gave 97.5% Cl_3SiCH_2-$CHClCH_2Cl$, b_{747} 208.5°, 1.4886, 1.4726 (Raman spectrum: 170(8), 203(5), 245(5), 257(2), 306(4), 336(9), 378(5), 387(5), 455(1), 480(4), 472(2), 496(5), 514 (1), 579(1), 596(1), 650(2), 686(5), 672(5), 705(5), 740(4), 755(5), 808(6), 815(8), 875(0), 1010(0), 1086(1), 1128(1), 1175(1), 1265(2), 1281(5), 1298 (5), 1354(0), 1354(1), 1398(2), 1440(2), 1552(0), 1615(4), 2900(5), 2940(5), 2966(4), 3008(1). This (105 g.) distd. from 1 g. $AlCl_3$ gave 62% Cl_3SiCH_2-$CH{:}CHCl$, b_{745} 165.5°, 1.4720, 1.3875; if dehydrochlorination is run with

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quinoline, there are formed two substances in 1:4 ratio, one of which b_{748}166 1.4790, 1.3923, and the second, b_{748}178.5°, 1.4885, 1.3969; structures of these were not detd. Treatment of the trichloro deriv.above with MeMgCl gave 65.5% $Me_3SiCH_2CH{:}CHCl$, b_{736}157.5°, 1.4445, 0.8978 (Raman spectrum, 166(4), 215(5), 224(3), 242(5), 280(5), 445(5), 545(4), 602(10), 664(5), 700(4), 760 (4), 770(1), 808(0), 855(2), 919(2), 1040(0), 1157(10), 1251(8), 1255(1), 1417(4), 1470(1), 1625(8), 2840(1), 2888(10), 2960(9), 3000(4), 3064(4)). Reaction of 10 g. Na, 20 g. Me_3SiCl and 25.5 g. $Me_3SiCH_2CH{:}CHCl$ gave 39% $Me_3SiCH_2CH{:}CHSiMe_3$, b_{755}171°, 1.4390, 0.7606(Raman spectrum: 170(4), 216(5), 242(4), 295(2), 422(4), 578(10), 590(2), 614(5), 654(5), 695(5), 706(2), 767 (5), 802(1), 845(3), 858(3), 1130(8), 1237(5), 1260(5), 1321(1), 1419(4), 1600(8), 2841(1), 2898(10), 2958(10)). Reaction of 476 g. $Cl_3SiCH_2CHClMe$ and 550 g. Sb_2Cl_2 with 1.5 g. Bz_2O_2 added in 3 portions gave 80.5% dichloropropyltrichlorosilane, $b_7$60-90°, which dehydrochlorinated with quinoline to 87.5% mixed chloropropenyltrichlorosilanes, b.157-65°, which with MeMgCl gave mixed chloropropenyltrimethylsilanes, b.132-6°, 1.4445, 0.8947, whose Raman spectrum was: 210(5), 244(1), 278(2), 357(1), 398(9), 445(0), 480(0), 514(0), 560(9), 627(10), 697(5), 755(2), 795(0), 840(0), 849(0), 991(0), 1030(0), 1255(2), 1280(4), 1528(0), 1378(3), 1416(3), 1459(2), 1521(0), 1564(1), 16214 (10), 2854(3), 2900(10), 2922(8), 2963(10), 3015(3), 3045(1), 3071(1); this condensed by means of Na with Me_3SiCl gave mixed disilanes $C_9H_{22}Si_2$, b_{755} 176-7°, 1.4545, 0.8005, whose Raman spectrum was: 166(1), 259(0), 273(0), 293(5), 303(5), 586(1), 645(10), 688(5), 734(0), 804(0), 1022(0), 1257(1), 1301(0), 1360(4), 1375(1), 1446(1), 1517(0), 1575(5), 1607(1), 2847(1), 2901 (10), 2960(10). The product described by Petrov and Shchukova (Zhur.Obsh.Khim. 26,353(1956)) as possibly $Me_3SiCH{:}CHSiMe_3$ is shown to be $(Me_3Si)_2C{:}CHMe$ on the basis of Raman spectra. Also reported are: $Cl_3SiCHClEt$, b_{737}156°, 1.4595, 1.5436; $Cl_3SiCH_2CHClMe$, b_{744}162°, 1.4600, 1.5410; $Cl_3SiCH_2CH_2CH_2Cl$, b_{760}116°, 1.4455, 1.2285; $Cl_3SiCMe{:}CH_2$, [illegible] b_{760}116°, 1.4455,1.2285 and $Cl_3SiCHMeCH_2Cl$, b_{752}191°, 1.4670, 1.4711.

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Thermal telomerization of olefins with silanes containing Si-H bond. A.N.Nesmeyanov, R.Kh.Freidlina and E.Ts.Chukovskaya (Inst.Hetero-Org. Compounds, Acad.Sci.,Moscow). Doklady Akad.Nauk S.S.S.R. 115,734-6(1957). Heating in autoclave 90 g. Et_3SiH with C_2H_4 at 300° at 200 atm. 4 hrs. gave 60 g. starting material, 15 g. Et_4Si and 8 g. Et_3SiBu, b_{50} 89-93°, n_D^{20} 1.4360, d_{20} 0.7810, along with a mixed fraction, b_4 70-110°. Similar reaction of $PhSiHCl_2$ and C_2H_4 in 3 hrs. at 280-300° at 60 atm. gave $PhEtSiCl_2$, $PhBuSiCl_2$ and $C_6H_{13}SiPhCl_2$, the properties of these fractions being,resp. b_7 84°, n_D^{20} 1.5180, d_{20} 1.1490; b_3 90-1°, 1.5140, 1.1181; and b_3 115-8°, 1.5100, 1.0832. Reaction of $(EtO)_3SiH$ with C_2H_4 was observed similarly at about 300° but individual products could not be isolated.

Organosilicon

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Reaction of dialkylchlorosilanes with aluminum chloride.
B.N.Dolgov, S.N.Borisov and M.G.Voronkov (State Univ.,Leningrad). Zhur. Obshchei Khim.27, 2062-6(1957). Cf. this j.27,709(1957) and Brit.663,810. Distn. of R_2SiHCl with 8-10 mole % $AlCl_3$ leads to disproportionation which may be summarized as: $5\ R_2SiHCl \rightarrow RSiH_3 + R_2SiH_2 + 2\ R_2SiCl_2 + R_3SiCl$. The reaction affords a convenient synthesis of R_2SiH_2. With larger amounts of the catalyst the reaction proceeds further, yielding R_3SiCl which is formed in satisfactory yield. The necessary R_2SiHCl were prepd. from RMgBr and $RSiHCl_2$ in 28-32% yields. Et_3SiH formed in 55-70% yield from EtMgBr and 0.5 mole $EtSiHCl_2$. Distn. of 30.9 g. Et_2SiHCl from 3.1 g. $AlCl_3$ gave 3.8 g. Et_2SiH_2, 7 g. starting material, and 12.3 g. Et_2SiCl_2. Distn. of 29.4 g. Et_2SiHCl from 6.4 g. $AlCl_3$ gave 1 g. Et_2SiH_2, 1.9 g. starting material, and 6.8 g. Et_3SiCl. MePrSiHCl (20.5 g.) distd. from 1.8 g. $AlCl_3$ gave 3 g. $MePrSiH_2$, 5.8 g. starting material and 7.4 g. $MePrSiCl_2$. Distn. of 36.4 g. iso-PrSiMeHCl from 4 g. $AlCl_3$ gave 3.7 g. iso-$PrSiMeH_2$, 14.8 g. unreacted material and 12.9 g. iso-$PrSiMeCl_2$. Similarly 85.3 g. Et_2SiCl_2 distd. from 14.5 g. $AlCl_3$ after refluxing 31 hrs. gave 96.2% starting material. To a refluxing mixture of 45.5 g. Et_3SiH and 0.8 g. $AlCl_3$ was added over 2 hrs. 31.4 g. Et_2SiH_2 and after refluxing 2.5 hrs. longer the mixture was distd. yielding 4.5 g. Et_2SiH_2 and 59.1 g. Et_3SiCl. Distn. of 38.2 g. Et_3SiH, 0.68 g. $AlCl_3$ and 25.8 g. Et_2SiCl_2 gave 7.6 g. Et_2SiH_2 and 48.7 g. Et_3SiCl in a 2.5 hrs. run. Following constants are reported: Et_2SiHCl, b.100.7°, n_D^{20}1.4152, d_{20}0.8895; MePrSiHCl, b.95.9°, 1.4098, 0.8796; iso-PrSiMeHCl, b.90.6°, 1.4173, 0.8928; Et_2SiH_2, b.55.7°, 1.3916, 0.6837; $MePrSiH_2$, b. 53.6°, 1.3857, 0.6798; iso-$PrSiMeH_2$, b.51.7°, 1.3789, 0.6697; Et_2SiCl_2, b.128.2°, 1.4307, 1.0475; $MePrSiCl_2$, b.124.4°, 1.4250, 1.0351; iso-$PrSiMeCl_2$, b.121.2°, 1.4270, 0.0385; Et_3SiH, b.107.5°, 1.4120, 0.7316; Et_3SiCl, b.146.8°, 1.4308, 0.8885.

Photochemical chlorination of ethylfluorosilanes. Orienting effect of fluosilyl group.
V.A.Ponomarenko and A.D.Snegova (Inst.Org.Chem.,Acad.Sci.,Moscow). Zhur. Obshchei Khim.27, 2067-73(1957). Cf. P. et al. Izvest.Akad.Nauk SSSR, otd. khim.nauk 1957, 310.
Increase of the number of F atoms at Si in a series of fluosilanes leads to increased tendency toward β-orientation by the fluosilyl group. Et_2SiF_2, from Et_2SiF_2 and HF, $b_{742.5}$61.5-2°, d_{20}0.9357, n_D^{20}1.3398. Heating $EtSiCl_3$ with CoF_2 in iso-octane gave $EtSiF_3$, b_{741}-5°. Chlorination for 27 hrs. of Et_2SiF_2 (for method cf. Petrov et al. Doklady Akad.Nauk SSSR 100,1107(1955)), gave 42 unreacted material, 30% $MeCHClSiEtF_2$, $b_{753.2}$103.2°, 1.1155, 1.3790,

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35% $ClCH_2CH_2SiEtF_2$, $b_{751.1}$ 135.5°, 1.1467, 1.3900, and a little $Cl_2C_2H_3SiEtF_2$, $b_{751.1}$ 148.2°, 1.3099, 1.4207. Similar chlorination of $EtSiF_3$ for 7.5 hrs. gave some starting material, 7.4% $MeCHClSiF_3$, $b_{749.5}$ 39.5°, 1.2606, 1.3180, 32.4% $ClCH_2CH_2SiF_3$, $b_{749.5}$ 68.5°, 1.3661, 1.3418, and some $Cl_2C_2H_3SiF_3$, $b_{749.5}$ 91.7-2°, 1.5007, 1.3750. Chlorination of 192.5 g. $MeCHClSiCl_3$ over 8 hrs. up to 179° gave 20.9% $MeCCl_2SiCl_3$, b_{738} 152°, m.109-11°, and 17.4% $ClCH_2CHClSiCl_3$, b_{732} 179°, 1.5207, 1.4835. Similar chlorination of $ClCH_2CH_2SiCl_3$ for 31 hrs. gave some starting material, 51.5% mixed $ClCH_2CHClSiCl_3$ and $Cl_2CHCH_2SiCl_3$, b_{18} 69°, 1.5908, 1.4808, and 4.4% mixed $Cl_3C_2H_2SiCl_3$, b_{17} 80.5°, 1.5908, 1.4910. Redistn. of the above mixture gave mainly $Cl_2CHCH_2SiCl_3$, $b_{742.5}$ 174.5°, 1.5214, 1.4798, and very little $ClCH_2CHClSiCl_3$, b_{750} 180°, n_D^{20} 1.4844. Chlorination of 115 g. 1,1,1,3-tetrachloropropane as above up to 184° over 32 hrs. gave 7.3g. starting material, 46.1% 1,1,1,3,3-pentachloropropane, b_{24} 79°, 1.5736, 1.4980, and 14.3% 1,1,1,2,3-pentachloropropane, b_{21} 85.5-6°, 1.6064, 1.5078. Heating 35 g. $ClCH_2CH_2SiEtF_2$ with 35 g. quinoline gave a vigorous gas evolution and yielded 9 g. liquid product from which were isolated 3.1 g. $EtSiCl_3$ and apparently 1.6 g. $CH_2:CHSiEtCl_2$. Similar reaction of $MeCHClSiEtF_2$ with quinoline proceeded smoothly and gave 5.3% $CH_2:CHSiEtF_2$, b_{742} 56°, 0.9578, 1.3346, and much starting material.

Synthesis of alkylalkoxyacetoxysilanes. organosilicon

K.A.Andrianov, A.A.Zhdanov and A.A.Bogdanova (Inst.Hetero-org.Compounds, Acad.Sci.,Moscow). Zhur. Obshchei Khim.27, 2073-5(1957). Cf. Doklady Akad.Nauk SSSR 108,83(1956), and 94, 697(1954).

To 65 g. $MeSi(OAc)_3$ was added over 25 min. 26 g. iso-AmOH and after 1 hr. at 54° there was obtained some 53 g. $(iso\text{-}AmO)SiMe(OAc)_2$, b_{10} 106-8°, d_{20} 1.0220, n_D^{20} 1.4065. Similarly double amount of ROH gave $(iso\text{-}AmO)_2SiMeOAc$, b_{14} 129-30°, 0.9269, 1.4083. Similarly, 88 g. $Me_2Si(OAc)_2$ and 31 g. $(CH_2OH)_2$ gave 31 g. $[Me_2Si(OCH_2)_2]_2$ b_{20} 85-130°(crude), which solidified on cooling, and whose suggested structure is $Me_2Si(OCH_2CH_2O)_2SiMe_2$. To 563.5 g. $ClCH_2CH_2OH$ and 8.5 g. Cu_2Cl_2 at 110-5° was added 378 g. $CH_2:CMeCO_2Na$ and 8.5 g. Cu_2Cl_2 which gave after 6-7 hrs. at 120° a range of products including unstated yield of ethylene monomethacrylate, b_{26} 99-103°. This with $MeSi(OAc)_3$, treated as above, gave among other products an unstated yield of readily polymerizable $MeSi(OAc)_2OCH_2CH_2O_2CCMe:CH_2$, $b_{0.5}$ 133-4°, 1.1516, 1.4335.

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Chlorination and bromination of phenyltrichlorosilane and the Raman spectra of halo-substituted phenyltrichlorosilanes.

A.D.Petrov, M.I.Batuev, V.A.Ponomarenko, A.D.Snegova, A.D.Matveeva and B.A.Sokolov (Inst.Org.Chem., Acad.Sci.,Moscow). Zhur. Obshchei Khim. 27, 2057-61(1957). Cf. this j.26, 1229(1956). Chlorination of $PhSiCl_3$ in the presence of ultraviolet light gave a mixture of 25% o-, 60% m-, and 15% p-$ClC_6H_4SiCl_3$ isomers. Chlorination at 70° in the presence of powd.Fe gave a mixture of isomers which after careful distn. were found to be: 24% o-isomer, 74% m-isomer, and 2% p-isomer (cf. Yakubovich et al. this j.26,568(1956)), as well as a dichloro deriv. of undetd. structure which b_{729} 264.5-4.8°, d_{20} 1.5528, n_D^{20} 1.5641. Bromination of $PhSiCl_3$ in the presence of powd.Fe at 62-5° gave 31% o-$BrC_6H_4SiCl_3$, 31% m-isomer and 38% p-isomer. Pure substances, prepd. by the Grignard route were found to have the following characteristics: o-$ClC_6H_4SiCl_3$, $b_{742.5}$ 240.5°, d_{20} 1.4629, n_D^{20} 1.5510, Raman spectrum in cm^{-1}: 157(4), 188(7), 207(5), 268(2), 319(5), 353(0), 385(6), 438(9), 526(4), 571(3), 590(3), 601(3), 618(3), 666(4), 685(0), 719(0), 750(0), 869(0), 895(0), 1039(10), 1123(5), 1137(2), 1164(4), 1255(0), 1279(1), 1355(0), 1423(0), 1457(0), 1561(2), 1584(6), 2965(2), 2987(2), 3066(9), 3121(3), 3161(1). m-isomer, b_{738} 230.5°, 1.4384, 1.4581, Raman spectrum: 155(7), 188(6), 193(5), 234(4), 248(4), 340(9), 356(9), 427(4), 518(6), 578(3), 599(3), 608(3), 620(1), 670(4), 790(0), 996(10), 1029(2), 1079(3), 1102(1), 1117(1), 1138(5), 1178 (2), 1247(0), 1296(3), 1396(3), 1428(0), 1563(3), 1585(7), 3062(9), 3077 (1), 3119(3), 3163(2). p-isomer, $b_{745.5}$ 232.5°, 1.4316, 1.5418, Raman spectrum: 172(6), 190(3), 243(1), 316(6), 340(2), 369(0), 452(6), 578(4), 596 (2), 609(2), 621(0), 634(2), 719(0), 754(4), 1067(2), 1091(10), 1119(10), 1160(0), 1191(3), 1224(0), 1273(0), 1307(2), 1385(0), 1416(0), 1568(1), 1586(10), 2854(1), 2917(1), 2986(1), 3032(1), 3047(3), 3065(8), 3135(1), 3158(2). o-$BrC_6H_4SiCl_3$, $b_{768.5}$ 261-1.5°, 1.6956, 1.5710, Raman spectrum: 87(6), 108(5), 141(3), 184(4), 198(3), 263(2), 285(3), 373(10), 521(4), 579(3), 589(3), 601(3), 623(1), 654(4), 1028(3), 1043(9), 1115(4), 1132(4), 1168(5), 1249(1), 1275(1), 1296(1), 1398(1), 1424(1), 1557(4), 1581(6), 1610(0), 1634(0), 2827(0), 2868(0), 2907(0), 2927(0), 2971(0), 3050(4), 3062(7), 3077(3), 3087(0), 3120(2), 3140(0), 3157(1). m-Isomer, b_{746} 251.4-1.7°, 1.6484, 1.5635, Raman spectrum: 154(5), 186(3), 221(2), 244(0), 262(0), 282(6), 304(4), 319(2), 409(8), 547(7), 582(3), 595(3), 607(3), 622(1), 633(3), 714(0), 739(6), 1071(10), 1112(4), 1123(5), 1191(5), 1291(1), 1306(1), 1355(0), 1393(0), 1416(0), 1547(0), 1577(10), 1607(0), 1627(0), 1663(0), 2855(1), 2959(2), 3001(2), 3024(2), 3046(6), 3064(10), 3082(3), 3102(3), 3155(3). The amount of m-Br isomer stated above was detd. by difference.

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antimony

New method of preparation of aromatic antimony compounds.

P.G.Sergeev and A.B.Bruker. Zhur.Obshchei Khim.27, 2220-3(1957). Cf. this j.7,1880(1937), 18,1297(1948).2

To a soln. of 57.1 g. $SbCl_3$, 42.5 g. $CuCl_2$, 100 ml. concd.HCl and 200 ml.H_2O was added 27 g. $PhNHNH_2$ and the mixture was stirred 5 hrs. in contact with air, yielding a pink ppt. which was sepd. and thoroughly washed with dil. HCl and Me_2CO; the Me_2CO ext. after addn. of Et_2O and H_2O gave 15-18% diphenylstibonic acid, which in 1:2 HCl gave Ph_2SbCl_3, m.175°, which in warm dil.HCl was treated with EtOH, filtered and treated with 1-2 crystals of KI and a stream of SO_2 yielding 77% Ph_2SbCl, m.69-70°. The filtrates f diphenylstibonic acid perpn. above were treated with NH_4Cl in concd.HCl yielding on cooling $PhSbCl_4.NH_4Cl$, a sparingly sol.solid, obtained in 2 yield, which with H_2O gave phenylstibonic acid, which with 1:1 HCl, a l KI and a stream of SO_2 was converted to 58% $PhSbCl_2$. The probable mec of the initial reaction is discussed.

Synthesis of aromatic ~~xxxxxxxxx~~ compounds of antimony. VII. Preparation of p-fluorophenyl derivatives of antimony.

organoantimony

A.B.Bruker. Zhur.Obshchei Khim.27, 2223-6(1957).

To 28.5 g. $SbCl_3$ and 21.2 g. $CuCl_2$ in dil.HCl was added 16 g. $p\text{-}FC_6H_4NHNH_2$ and the mixture stirred 3-4 hrs. yielding a ppt. which after washing with dil.HCl was dissolved in Me_2CO(much N_2 is evolved), the filtrate being dild. with Et_2O and H_2O to yield 14-16% p,p'-bis(fluorophenyl)stibonic acid,does no m.250°; this with 1:1 HCl gave $(p\text{-}FC_6H_4)_2SbCl_3$, m.100°, resolit.149-50°, which with warm 1:1 HCl, a little KI and a stream of SO_2 was converted to $(p\text{-}FC_6H_4)$ $SbCl_2$, m.55°, which with 5% NH_4OH gave$[(p\text{-}FC_6H_4)_2Sb]_2O$, m.88°. The acidic filtrate from prepn. of R_2SbCl_3 on stirring 3-4 hrs. longer gave after addn. of NH_4Cl and concd.HCl a double salt $(p\text{-}FC_6H_4)SbCl_4.NH_4Cl$, which with H_2O gave 15% p-fluorophenylstibonic acid, does not m.250°. This with aq.HCl gave after treatment with SO_2 in presence of a little KI and extn. with Et_2O, an unstated yield of $p\text{-}FC_6H_4SbCl_2$, m.46-7°, which with 5% NH_4OH gave $p\text{-}FC_6H_4SbO$, [illegible], which with AcOH gave an acetate, m.120-1°.

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